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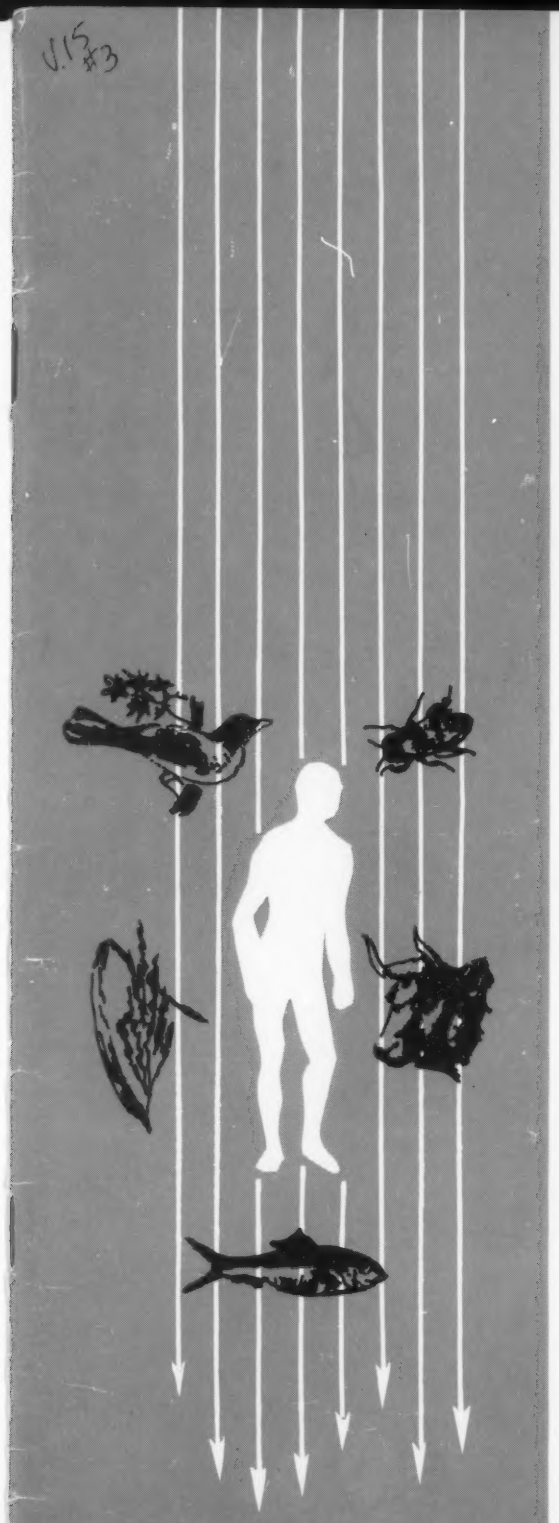

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CONTENTS

Volume 15 December 1981 Number 3

Page

FISH, WILDLIFE, AND ESTUARIES

Factors Influencing Dieldrin and DDT Residues in Carp from the Des Moines River, Iowa, 1977–80 ——— 111
Wayne H. Hubert and Edward D. Ricci

Influence of a New Impoundment on Pesticide Concentrations in Warmwater Fish, Saylorville Reservoir, Des Moines River, Iowa, 1977–78 ——— 117
Siu-Yin Theresa Leung, Ross V. Bulkley, and John J. Richard

Polychlorinated Biphenyls in Clams and Oysters from New Bedford Harbor, Massachusetts, March 1978 ——— 123
Walter I. Hatch, Donald W. Allen, Phillips D. Brady, Alan C. Davis, and John W. Farrington

Nationwide Residues of Organochlorine Compounds in Wings of Adult Mallards and Black Ducks, 1979–80 ——— 128
Brian W. Cain

HUMANS

Organochlorine Pesticide Residues in Human Milk Samples from Comarca Lagunera, Mexico, 1976 ——— 135
L. Albert, P. Vega, and A. Portales

WATER

1,2-Dibromo-3-chloropropane Residues in Water in South Carolina, 1979–80 ——— 139
George E. Carter, Jr., and Melissa B. Riley

APPENDIX ——— 143

ERRATUM ——— 144

Information for Contributors ——— 145

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The Monitoring Panel consists of representatives of the Agricultural Research Service, Animal and Plant Health Inspection Service, Extension Service, Forest Service, Department of Defense, Fish and Wildlife Service, Geological Survey, Food and Drug Administration, Environmental Protection Agency, National Marine Fisheries Service, National Science Foundation, and Tennessee Valley Authority.

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FISH, WILDLIFE, AND ESTUARIES

Factors Influencing Dieldrin and DDT Residues in Carp from the Des Moines River, Iowa, 1977–80[1]

Wayne H. Hubert and Edward D. Ricci[2]

ABSTRACT

Concentrations of dieldrin and DDT in muscle tissue and fat of carp, Cyprinus carpio, *from the Des Moines River, Iowa, differed significantly with month of collection, fish age, and sampling location. Pesticide levels expressed on the basis of wet weight of flesh often differed from those expressed on a fat basis. Fish from reservoirs tended to have higher levels of dieldrin, but not of DDT, than did fish from riverine locations.*

Introduction

Interpretation of data from organochlorine pesticide residue monitoring programs for freshwater fish is difficult because numerous factors influence sample variability. Identification of the factors that contribute to sample variability would improve the reliability of monitoring programs. Authors assessed the influence of selected variables in concentrations of aldrin and DDT in carp *(Cyprinus carpio)* from a midwest river, the Des Moines.

Aldrin and DDT were extensively used to control insects on midwestern cropland for many years. About 3 million kg of aldrin was applied to Iowa cropland in the mid-1960's to control corn rootworm and cutworm (*16*). The U.S. Environmental Protection Agency canceled registration of aldrin in 1975, and its use was discontinued in 1978. The pesticide DDT was used primarily to control European cornborer, Dutch elm disease, and mosquitoes during the 1950's and 1960's; it use was banned in 1970.

Both aldrin and DDT convert to persistent forms in nature, dieldrin and DDE or TDE, respectively. These compounds have long half-lives under field conditions—8–10 years for dieldrin and 10–20 years for DDE (*13, 15*)—and tend to be strongly adsorbed to soil particles (*7, 14*). Because of these factors and the widespread use of these compounds on cropland, midwestern waters continue to be contaminated through soil erosion. Chlorinated hydrocarbons, being hydrophobic, lipophilic chemicals, are absorbed from water into the fat of fish.

The Des Moines River is the largest stream within Iowa. More than 80% of its drainage is cultivated, and the major source of contamination of the river is nonpoint agricultural runoff (*9*). Two reservoirs have been constructed on the river for flood control, water quality control, and recreational purposes. Red Rock Dam, completed in 1969, impounds 4,200 ha of water at normal pool level. Saylorville Dam, completed in 1977, impounds 2,200 ha at normal pool level. A pesticide monitoring program was established on the Des Moines River in 1977, and several fish species were assessed for organochlorine pesticide residues from 1977 to 1979 (*2, 3, 12*). The cost of monitoring several species led to consideration of limiting analysis to a single sentinel species. Carp were selected because they are abundant and easy to collect in both the river and reservoirs. The objectives of the present paper are to compare wet weight of flesh- and fat-based units of measure for dieldrin and ΣDDT residues in carp; to assess the influence of sampling month, fish age, and sampling location in the river on residue concentrations; and to evaluate trends in dieldrin and ΣDDT residue concentrations in Des Moines River carp from 1977 to 1980.

[1] Journal Paper No. J-10204 of the Iowa Agriculture and Home Economics Experiment Station, Ames, IA. Project No. 2465. Financed by a grant from the U.S. Department of Defense, Army Corps of Engineers, and made available through the Engineering Research Institute, Iowa State University, to the Iowa Cooperative Fishery Research Unit.

[2] Iowa Cooperative Fishery Research Unit, Iowa State University, Ames, IA 50011. The Unit is jointly supported by Iowa State University, the Iowa State Conservation Commission, and the Fish and Wildlife Service, U.S. Department of the Interior.

Methods

Sampling stations were established at two impounded and two riverine locations on the Des Moines River (Figure 1): Red Rock Reservoir; the river 80 km upstream from Red Rock Reservoir at Des Moines; Saylorville Reservoir; and the river 80 km upstream from Saylorville Dam at Boone. Carp were collected from each location by electrofishing and hoop netting. Five samples were made up from each sampling location in June and in September. Each sample consisted of equal weights of lateral muscle from 10 fish of the same age. Fish ages were determined by standard scale-reading techniques (*11*); only 2- to 4-year-old fish were used. Fat content of individual samples was determined by the modified Babcock method (*1*).

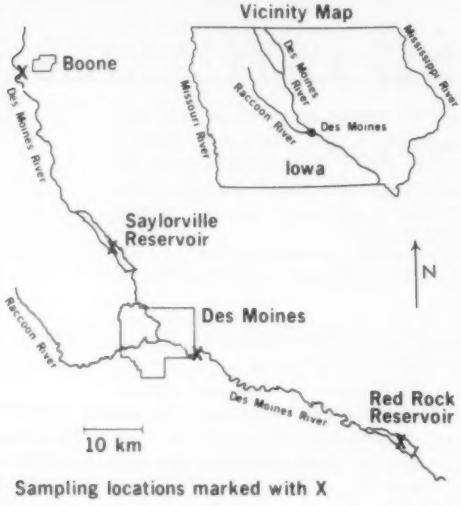

FIGURE 1. *Sampling stations for carp on the Des Moines River, Iowa.*

Lateral muscle tissue samples were analyzed for dieldrin, *p,p'*-DDT, *p,p'*-TDE, and *p,p'*-DDE by the methods described in the *Pesticide Analytical Manual* (*8*). Tissue samples were ground in a 35% water–acetonitrile solution with a high-speed blender for 10 minutes. The sample was filtered, the filtrate was transferred to a 1-liter separatory funnel, 100 ml petroleum ether was added, and the mixture was shaken briefly. Then, 600 ml distilled water and 10 ml saturated saline solution were added and mixed by tumbling for 1 minute. After the layers had separated, the aqueous fraction was discarded. The solvent layer was washed with distilled water and filtered through a 50-cm anhydrous sodium sulfate column. The sample volume was recorded, and the extract was subjected to the standard Florisil cleanup procedure (*8*).

A Tracor 550 gas chromatograph equipped with a ^{63}Ni electron-capture detector was used for gas chromatographic analysis. A 4% SE-30/6% SP-2401 column was used for separating and quantifying the pesticides. Detected values were corrected for 80% extraction efficiency.

Statistical procedures included the Student's *t*-test and the Pearson Product Movement Correlation Coefficient. All decisions to reject null hypotheses were at $P < 0.10$, because sources of variability were being sought.

Results

FAT IN CARP MUSCLE

Fat content of carp muscle ranged from 0.8% to 3.3% (Table 1). Between June and September, fat content of fish decreased significantly at the two riverine sites, Des Moines ($0.10 > P > 0.05$) and Boone ($0.01 > P > 0.001$), increased significantly in Saylorville Reservoir fish ($0.3 > P > 0.01$), and did not change significantly in Red Rock Reservoir fish. Fat content differed significantly between fish samples from Saylorville Reservoir and those from the river at Boone in both June and September. Fat levels were higher in river fish in June ($0.02 > P > 0.01$) and in reservoir fish in September ($0.01 > P > 0.001$). These demonstrated variations in fat content indicated the need to consider this variable in the pesticide residue analyses.

TABLE 1. *Fat content of carp muscle used for pesticide analysis from the Des Moines River, Iowa, 1980*

Month of Collection	Carp Age, Years	Percent Fat: Red Rock Reservoir	River at Des Moines	Saylorville Reservoir	River at Boone
June	3	1.5	1.8	1.4	1.8
		1.8	1.9	1.6	1.9
		2.3	2.2	1.6	2.3
	4	1.7	2.2	1.4	1.8
		1.9	3.3	—	2.4
(Mean)		(1.8)	(2.3)	(1.6)	(2.0)
Sept.	2	1.4	1.6	1.8	0.8
		1.1	2.0	2.4	1.1
	3	1.9	1.3	1.7	1.2
		2.6	1.4	2.5	1.6
	4	1.7	1.8	2.2	1.6
(Mean)		(1.7)	(1.6)	(2.1)	(1.3)

DIELDRIN

In 1980, concentrations of dieldrin ranged from 10 to 128 μg/kg of flesh and from 630 to 5,790 μg/kg of fat (Table 2). Mean levels of dieldrin in flesh and in fat declined between June and September at the four sampling locations. The differences in mean levels were statistically significant at Red Rock Reservoir ($0.10 > P > 0.05$), the river at Des Moines ($0.10 > P > 0.05$),

TABLE 2. *Dieldrin residues in muscle of carp from the Des Moines River, Iowa, 1980*

Month of Collection	Carp Age, Years	Residues, μg/kg							
		Red Rock Reservoir		River at Des Moines		Saylorville Reservoir		River at Boone	
		Flesh [1]	Fat	Flesh [1]	Fat	Flesh [1]	Fat	Flesh [1]	Fat
June	3	83	4,580	30	1,360	33	2,850	41	2,170
		73	3,150	55	3,060	51	2,030	41	1,790
		63	4,170	33	1,710	54	3,840	50	2,780
		—	—	—	—	56	3,520	—	—
	4	75	4,410	55	3,860	34	2,410	48	2,760
		110	5,790	128	2,500	—	—	66	2,640
(Mean)		(81)	(4,420)	(60)	(2,500)	(46)	(2,930)	(49)	(2,430)
Sept.	2	34	3,070	11	630	29	1,600	16	2,030
		53	3,750	15	750	43	1,770	21	1,930
	3	58	3,090	10	770	36	1,450	15	1,250
		59	2,210	41	2,950	45	2,650	24	1,480
	4	84	4,930	23	1,250	30	1,360	36	2,270
(Mean)		(58)	(3,410)	(20)	(1,270)	(37)	(1,770)	(22)	(1,790)

[1] Wet-weight basis.

and the river at Boone ($0.01 > P > 0.001$) when expressed on a wet-weight flesh basis. On a fat basis, the differences were statistically significant in the river at Des Moines ($0.10 > P > 0.05$), the Saylorville Reservoir ($0.05 > P > 0.02$), and the river at Boone ($0.05 > P > 0.02$).

Statistically significant variation in mean dieldrin level related to fish age was noted in June ($0.10 > P > 0.05$) but not in September, when wet-weight flesh was used as the analytical basis. No statistically significant variation due to age was observed in either June or September on a fat basis.

Differences in mean levels of dieldrin in carp samples occurred between some sampling locations. In June, no significant differences occurred between the reservoirs and their associated riverine stations when concentrations were expressed on a flesh basis, but a significantly higher level was observed in Red Rock Reservoir fish compared with fish from the river at Des Moines ($0.02 > P > 0.01$) on a fat basis. In September, dieldrin concentrations in fish were significantly higher at both Red Rock and Saylorville reservoirs than at the upstream locations ($0.01 > P > 0.001$ and $0.05 > P > 0.02$, respectively) on a flesh basis, but a significant difference was observed only between Red Rock Reservoir and the river at Des Moines on a fat basis.

Levels of dieldrin were significantly higher in samples from Red Rock Reservoir than in those from Saylorville Reservoir in June ($0.01 > P > 0.001$ for flesh, $0.05 > P >> 0.02$ for fat) and in September ($0.05 > P > 0.02$ for flesh, $0.02 > P > 0.01$ for fat). No significant differences were observed between riverine locations.

Trends in mean concentrations of dieldrin in carp muscle at the four sampling locations from 1977 to 1980 are illustrated in Figure 2. The 1977–79 samples were collected and analyzed in the same manner as described for 1980 samples. Size ranges of the fish indicate that the 1977-79 samples were predominantly composed of 2- and 3-year-old fish. Fish from the impounded sites tended to have higher levels of dieldrin than did those from the riverine sites (Figure 2). Substantial variation in dieldrin levels between sampling periods occurred at all locations, but the magnitude of the fluctuations was greatest in the reservoirs.

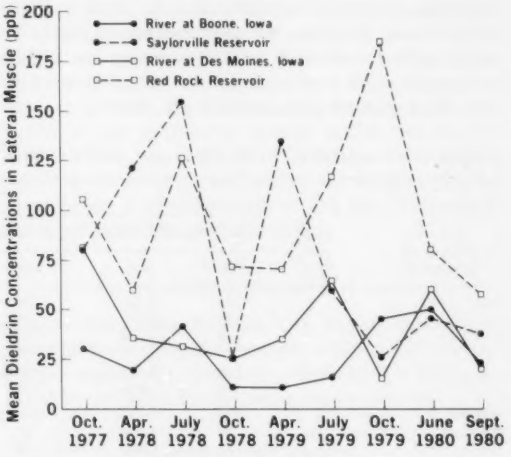

FIGURE 2. *Variation in dieldrin residues in flesh of carp from four sampling locations on the Des Moines River, Iowa, 1977–80. Data for 1977–79 taken from Baumann et al. (2, 3).*

TOTAL DDT

The concentration of ΣDDT (DDT, TDE, and DDE) in carp muscle ranged from 18 to 191 μg/kg of flesh and from 1,090 to 9,910 μg/kg of fat in 1980 samples (Table 3). In June, ΣDDT was composed of 54.8% DDE, 24.6% TDE, and 20.6% DDT in the average sample. Proportions were similar in September—53.3% DDE, 27.9% TDE, and 18.8% DDT.

ΣDDT levels in fish samples declined from June to September. The difference was statistically significant on a flesh basis at all sampling locations: Red Rock Reservoir ($0.02 > P > 0.01$), the river at Des Moines ($0.05 > P > 0.02$), Saylorville Reservoir ($0.10 > P > 0.05$) and the river at Boone ($0.01 > P > 0.001$). The concentration of ΣDDT in the fat was significantly lower in September only in fish from the reservoirs: Red Rock ($0.02 > P > 0.01$) and Saylorville ($0.05 > P > 0.02$).

The mean level of ΣDDT was significantly higher in 4-year-old fish than in 3-year-old fish on both flesh ($0.02 > P > 0.01$) and fat ($0.10 > P > 0.05$) bases in June. No differences among samples of 2-, 3-, and 4-year-old fish were observed in September.

Mean ΣDDT in carp varied significantly between some sampling locations. Concentrations were significantly higher in samples from Saylorville Reservoir than in samples from the upstream site near Boone in both June ($0.10 > P > 0.05$) and September ($P > 0.001$) on a flesh basis, but only in June on a fat basis ($0.02 > P > 0.01$). In September, mean level of ΣDDT was significantly higher in fish from the river at Des Moines than in fish from Saylorville Reservoir on both flesh ($0.10 > P > 0.05$) and fat ($0.01 > P > 0.001$) bases. This was the only comparison made in which the mean level of pesticide residues was higher in samples from a riverine location than in samples from the associated downstream impoundment.

Comparison of samples from the two reservoirs showed no significant differences in mean ΣDDT. However, statistically significant differences in mean ΣDDT occurred between fish from the two riverine sites in both June and September. Mean levels of ΣDDT were significantly higher in both flesh ($0.02 > P > 0.01$ in June, $0.01 > P > 0.001$ in September) and fat ($0.01 > P > 0.001$ in June, $0.01 > P > 0.001$ in September) of fish sampled near Des Moines than in those collected at Boone.

Mean ΣDDT concentration in carp samples declined substantially between October 1977 and July 1978 at the two riverine locations (Figure 3). ΣDDT levels in

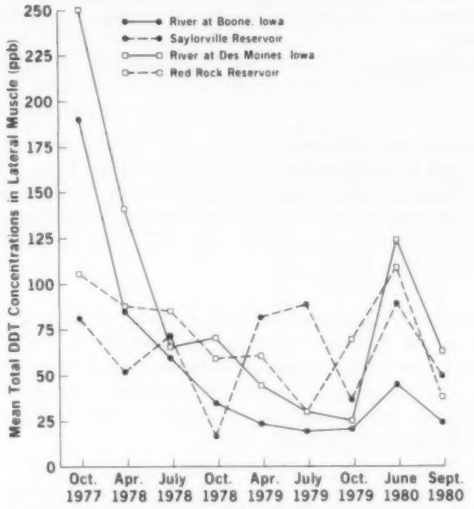

FIGURE 3. *Variation in total DDT residues in flesh of carp from four sampling locations on the Des Moines River, Iowa, 1977–80. Data for 1977–79 taken from Baumann et al. (2, 3).*

TABLE 3. *Total DDT (DDT, TDE, and DDE) residues in muscles of carp from the Des Moines River, Iowa, 1980*

Month of Collection	Carp Age, Years	Residues, μg/kg							
		Red Rock Reservoir		River at Des Moines		Saylorville Reservoir		River at Boone	
		Flesh	Fat	Flesh	Fat	Flesh	Fat	Flesh	Fat
June	3	55	4,240	83	3,980	96	4,720	35	2,890
		126	5,490	88	4,860	74	2,820	50	2,170
		76	2,670	88	4,340	46	5,270	55	1,560
		—	—	—	—	85	6,020	—	—
	4	149	7,650	191	4,810	185	9,910	28	1,830
		130	7,830	159	8,690	—	—	55	1,290
(Mean)		(107)	(5,780)	(122)	(5,340)	(97)	(5,760)	(45)	(1,950)
Sept.	2	31	2,230	51	3,200	40	2,920	28	2,500
		20	1,820	79	3,940	53	1,670	21	2,660
	3	41	2,170	43	3,270	53	2,150	23	1,880
		44	1,680	50	3,570	54	3,090	18	1,090
	4	56	3,310	91	5,070	43	1,930	29	1,800
(Mean)		(38)	(2,240)	(63)	(3,810)	(49)	(2,350)	(24)	(1,990)

carp have fluctuated substantially at all locations since 1978, with no indication of significant differences in trends between impounded and riverine locations.

Discussion

The lipophilic nature of organochlorine pesticide residues results in significant associations between fat content and pesticide levels in fish (*4, 5, 12*). It has been suggested that the variance in organochlorine pesticide residue samples may be reduced by normalizing on a fat basis. Statistically significant variation in fat content of Des Moines River carp was observed between sampling months, ages of fish, and sampling location, indicating a need to consider the fat content in data analyses. However, normalization on a fat basis in Des Moines River carp samples did not reduce the variability of the data. Comparisons of dieldrin and ΣDDT concentrations between sampling months, fish ages, and sampling locations produced results that were different on fat and flesh bases in several instances.

The mean levels of both dieldrin and ΣDDT in Des Moines River carp varied between sampling periods. A decline was observed between June and September 1980. Concentrations of dieldrin and ΣDDT in carp from the Des Moines River fluctuated dramatically between sampling periods from 1977 to 1979, but a spring-to-autumn decline did not consistently occur. During 1971–73, before the use of dieldrin was discontinued, seasonal trends in dieldrin concentrations in Des Moines River channel catfish (*Ictalurus punctatus*) were related to corn planting and aldrin application (*10*). Present patterns are more complicated and probably relate to several factors, including water temperature (and, consequently, metabolic rates of fish) before sampling (*6*), fat content of the fish (*4, 5*), extent of pesticide contamination in bottom sediments and on agricultural land within the watershed (*17*), tillage practices by farmers, and precipitation before sampling. The results indicate that evaluation of variations in organochlorine pesticide residues relative to sampling locations or time should be made on fish of the same age. The need to consider fish age was shown in June when levels of dieldrin and ΣDDT were significantly higher in 4-year-old than in 3-year-old fish. Similar variation relative to age has been described in channel catfish from the Des Moines River (*4, 5*).

The present study showed that impoundments within a river system may affect the data developed in a monitoring project. Dieldrin in carp muscle tended to be higher in fish from reservoirs than from upstream riverine sites, but the same trend did not hold consistently for ΣDDT. Whole-body analyses of carp in 1977 and 1978 showed no difference in either dieldrin or ΣDDT levels between Saylorville Reservoir and either upstream or downstream locations (*12*). Differences in dieldrin and ΣDDT occurrence relative to the impoundments indicated that the dynamics of the two types of pesticide residues are different within reservoirs. Differences also were noted between riverine and impounded locations.

Concentrations of dieldrin and ΣDDT in 1980 carp samples from the Des Moines River were below Food and Drug Administration, U.S. Department of Health and Human Services, standards of 300 ppb dieldrin and 5 ppm DDT for food fish. Dieldrin in some samples of channel catfish flesh from Des Moines River impoundments in 1977 (*6*) and 1979 (*3*) exceeded those standards, thereby indicating the need for monitoring as well as the need to define the relation between organochlorine pesticide residues in sentinel species, such as carp, and other fish species.

Analysis of 1977–79 data (*2, 3*) from the Des Moines River showed a significant correlation ($r = 0.51$, $0.02 > P > 0.01$) between mean levels of dieldrin in carp and channel catfish samples taken at the same time and location, but not between concentrations in carp and those in walleye (*Stizostedion vitreum vitreum*), or largemouth bass (*Micropterus salmoides*). From 1977 to 1979, the mean dieldrin level in channel catfish exceeded that of carp by 2.2 times in samples from Red Rock Reservoir and by 3.1 times in samples from Saylorville Reservoir; however, the factor varied substantially between sampling dates. Leung (*12*) found a positive correlation ($r = 0.56$) between percentage fat of various species found in the Des Moines River and dieldrin levels in the flesh. She noted that channel catfish tended to have double the fat content and triple the dieldrin concentrations of carp, but observed no similar relations in ΣDDT concentrations. The extent of the relation between species and fat content provides some basis for extrapolating dieldrin levels observed in carp to those in channel catfish, but not for ΣDDT or for other species. The relation between dieldrin levels in carp and catfish would probably be strengthened if variables such as fish age, fat content, and capture location were controlled.

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Influence of a New Impoundment on Pesticide Concentrations in Warmwater Fish, Saylorville Reservoir, Des Moines River, Iowa, 1977–78 [1]

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ABSTRACT

Samples of seven species of warmwater fish were collected above, within, and below newly impounded Saylorville Reservoir, Des Moines River, Iowa, from October 1977 to October 1978. Whole-body analyses by gas chromatography were significantly higher in river carpsucker (Carpiodes *cyanazine and for the organochlorine insecticides dieldrin, p,p'-DDE, p,p'-TDE, p,p'-DDT, and heptachlor epoxide. Only the organochlorine insecticides were detected in fish tissue. Concentrations of dieldrin and heptachlor epoxide were significantly higher in river carpsucker* (Carpiodes carpio) *from the reservoir than in those from the river. Other species of fish showed no differences in pesticide concentration related to locality of collection.*

Introduction

The construction of a reservoir on a river increases the complexity of pesticide dynamics in the aquatic system. Impoundments for flood control, water supplies, energy development, recreation, and other purposes are becoming increasingly numerous in the United States. During 1977–78, a study was conducted on Saylorville Reservoir, a new impoundment on the Des Moines River up stream from Des Moines, Iowa, to determine the rate of pesticide deposition in the reservoir and the effect of impoundment on pesticide accumulation in different species of fish. The discussion here addresses pesticide accumulation in the fish. Elsewhere, Leung (*6*) reported on seasonal pesticide fluctuations and pesticide deposition in the reservoir.

The Des Moines River rises in the glacial moraine area of southwestern Minnesota and flows southeasterly across Iowa to join the Mississippi (Figure 1). It is the largest river in Iowa. About 79% of the watershed upstream from Des Moines is cropland, primarily corn and soybeans; 6% is permanent pasture, 5% is forest, and 7% is urban (*4*). Normal annual precipitation over the drainage area ranges from 62.5 to 77.5 cm from north to south and averages 70.7 cm (*8*). Precipitation is usually heaviest in June, but heavy rainfall and cloudbursts occasionally cause high river flows in summer and early fall. The major source of contamination of the river is agricultural runoff.

FIGURE 1. *Upper Des Moines River watershed, showing sampling sites.*

Three collection stations were set up for this study: Station 1 at Boone, Iowa, is about 73 km upstream from Saylorville Dam; Station 2 is located in Saylorville Reservoir; and Station 3 is located at the town of Saylorville, about 3 km downstream from Saylorville Dam. Drainage areas at the three points, upstream to downstream, are 14,530, 15,081, and 15,128 km^2, respectively.

Gates on the Saylorville Reservoir were closed in April 1977. During the study period, the reservoir remained

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[1] This study was conducted as part of Project 2225 of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa, in cooperation with the Iowa Cooperative Fishery Research Unit, which is jointly sponsored by the Iowa State Conservation Commission, Iowa State University, and the Fish and Wildlife Service, U.S. Department of the 'nterior.

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within 1.2 m of conservation pool level, and average water retention time was about 40 days (*1*). Volume at conservation pool level was about 90 million m^3.

Materials and Methods

Fish samples were collected quarterly at Stations 1, 2, and 3 from October 1977 to October 1978, with gill nets, hoop nets, and electroshockers. Species analyzed for pesticide residues were gizzard shad *(Dorosoma cepedianum)*, river carpsucker *(Carpiodes carpio)*, common carp *(Cyprinus carpio)*, channel catfish *(Ictalurus punctatus)*, white crappie *(Pomoxis annularis)*, largemouth bass *(Micropterus salmoides)*, and walleye *(Stizostedion vitreum)*. Specimens were grouped by collection date, location, species, and body length. An attempt was made to collect small specimens and to avoid large, old fish of each species. Small fish were selected on the assumption that most of their life occurred after impoundment, and that they would be less likely than old fish to have migrated between sampling stations. With few exceptions, all fish selected for sampling were subadult, and many were young-of-the-year. Mean total lengths ranged from 137 mm for gizzard shad to 232 mm for walleyes (Table 1).

Fish in the same group were ground together in a hand grinder and then mixed manually in an effort to obtain a homogeneous mixture. Subsamples were then wrapped in aluminum foil and frozen until analysis. Because preliminary analyses indicated that atrazine, alachlor, cyanazine, dieldrin, *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, and heptachlor epoxide were present in water or fish, these substances were selected for study. Concentrations of pesticides in water are listed in Table 2.

TABLE 2. *Mean weekly dissolved pesticide concentrations (ng/liter) at each Des Moines River station where fish were collected, September 1977 to November 1978* [1]

Chemical	Station 1	Station 2	Station 3	Mean
Atrazine	225 (<10–1356)	221 (0–1167)	222 (<10–1000)	223
Alachlor	115 (0–1450)	80 (0–1125)	72 (0–725)	89
Cyanazine	71 (0–500)	90 (0–660)	111 (0–640)	91
Dieldrin	3 (0–14)	3 (<1–6)	3 (<1–6)	3
p,p'-DDE [2]	<1	<1	<1	<1

NOTE: Numbers in parentheses are ranges.
[1] Values are from Ref. 6.
[2] Mean concentration of *p,p'*-DDE on suspended sediment was 7 ng/kg (0–66) at Station 1, 4 ng/kg (0–25) at Station 2, and 6 ng/liter (0–132) at Station 3.

Authors used standard methods of tissue analysis (*7*) with slight modification. After thawing, 25–30-g samples were extracted with 200 ml of 65% acetonitrile–water for 5 minutes in a 1-liter stainless steel blender. The sample was then filtered into a 250-ml graduated

TABLE 1. *Number of fish and range in length of fish collected from the Des Moines River for pesticide residue analysis, 1977–78*

Station [1]	Date	Length, mm [2]						
		Gizzard Shad	River Carpsucker	Common Carp	Channel Catfish	White Crappie	Walleye	Largemouth Bass
1	Oct. 1977	45 (136–199)	33 (76–278)	64 (83–402)	0	0	4 (144–180)	1 (195)
	Apr. 1978	0	46 (85–328)	91 (85–130)	0	0	0	0
	Jul. 1978	0	58 (103–368)	42 (131–269)	34 (98–247)	13 (108–141)	19 (175–430)	8 (230–315)
	Oct. 1978	40 (146–205)	23 (152–400)	52 (140–272)	5 (154–413)	16 (132–170)	4 (180–279)	18 (120–348)
2	Oct. 1977	56 (104–163)	6 (131–307)	35 (103–191)	10 (310–487)	31 (75–295)	5 (160–300)	46 (95–260)
	Apr. 1978	6 (128–195)	6 (198–367)	69 (105–216)	17 (232–430)	4 (87–98)	3 (245–282)	6 (96–262)
	Jul. 1978	34 (67–212)	25 (177–381)	18 (155–241)	9 (285–457)	10 (137–305)	2 (350–351)	26 (123–387)
	Oct. 1978	63 (100–199)	27 (176–400)	39 (165–312)	8 (240–398)	7 (160–178)	0	23 (166–310)
3	Apr. 1978	0	22 (140–335)	40 (100–189)	0	46 (81–324)	0	0
	Jul. 1978	40 (56–101)	7 (140–290)	47 (135–238)	3 (220–290)	56 (112–332)	3 (202–286)	4 (246–310)
	Oct. 1978	93 (112–189)	49 (141–342)	39 (131–226)	0	34 (82–189)	0	0
	Total fish	377	302	536	86	217	40	132

[1] See Figure 1 for locations of stations.
[2] Range is in parentheses.

cylinder and transferred to a 1-liter separatory funnel; 100 ml petroleum ether, 600 ml water, and 10 ml saturated aqueous sodium chloride were added to the filtrate. The pesticides were partitioned into the organic layer by vigorous shaking for 30–60 seconds. The aqueous layer was discarded. The petroleum ether layer was washed with two 100-ml portions of water to remove the remaining acetonitrile and was transferred to a 100-ml graduated cylinder, and the recovered volume was recorded. The wet weight of a tissue sample was corrected for the losses of acetonitrile–water mixture and petroleum ether. The extracts were then subjected to Florisil column cleanup. The eluate was concentrated to 10 ml for quantification. Results were expressed in nanograms of pesticide per gram of fish tissue (parts per billion, wet-weight basis).

Instrument parameters and operating conditions for the quantification of (a) alachlor, cyanazine, dieldrin, *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, and heptachlor epoxide, and (b) atrazine follow:

Gas chromatograph:	Tracor 550
Detectors:	(a) ^{63}Ni electron capture (b) N-P
Columns:	glass, 4 mm id packed with 10% DC-200 on 80–100-mesh Gas-Chrom Q glass, 4 mm id packed with a mixture of 4% SC-30 and 6% OV-210 on 80–100-mesh Gas-Chrom Q
Temperatures:	detectors (a) 340° C (b) 240° C column 210° C
Carrier gas:	nitrogen flowing at 90–100 ml/min

Values were not corrected for the ca 80% recovery rate obtained in the extraction. Previous studies (5) and preliminary tests revealed little interference from polychlorinated biphenyls (PCBs) and chlordane. The majority of the PCBs were present as Aroclor 1242 or 1246, which did not interfere with the other pesticide analyses. No chlordane was observed in water or fish samples. Pesticide detection limits were about 10 μg/kg. Where necessary, authors transformed data on pesticide concentrations to log 10 values before conducting analysis-of-variance or *t*-tests or computing correlation coefficients.

Results

The herbicides atrazine, alachlor, and cyanazine were not detected in the fish samples. The insecticides dieldrin and *p,p'*-DDE were found in all samples, and heptachlor expoxide, *p,p'*-DDT, and *p,p'*-TDE were found in most. Dieldrin usually occurred in greater concentrations than did other insecticides. DDT occurred in lower concentrations than did its metabolite. Probably because the length of fish within samples was limited, no consistent relation was evident between pesticide concentration and body length in any species except largemouth bass ($r = 0.66$, $P = 0.01$). Therefore, data were pooled for each species except bass to compare location and time of year (Table 3).

Because gizzard shad, channel catfish, white crappies, and walleyes were not captured at each station on each

TABLE 3. *Monthly mean whole-body insecticide levels in seven species of Des Moines River fish, 1977–78*

Species	Station	Date	Number of Analyses [1]	Residues, μg/kg Wet Weight					
				Dieldrin		ΣDDT		Heptachlor Epoxide	
				Mean	Range	Mean	Range	Mean	Range
Gizzard shad	1	Oct. 1977	3	171	142–191	24	8–49	10	8–13
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	0	—	—	—	—	—	—
		Oct. 1978	2	112	87–137	71	71–72	16	12–21
		Mean		147		43		13	
	2	Oct. 1977	3	66	64–77	20	13–27	0	—
		Apr. 1978	1	119	—	188	—	10	—
		Jul. 1978	3	73	53–111	61	42–71	14	7–26
		Oct. 1978	3	143	132–157	54	52–59	17	15–19
		Mean		96		59		10	
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	1	14	—	31	—	2	—
		Oct. 1978	4	137	107–182	69	56–104	29	12–68
		Mean		113		61		21	
River carpsucker	1	Oct. 1977	4	44	24–58	72	49–99	0	—
		Apr. 1978	6	34	7–33	52	19–86	3	0–4
		Jul. 1978	4	58	11–114	40	10–64	7	0–13
		Oct. 1978	4	69	20–197	35	18–64	3	0–11
		Mean		49		50		3	
	2	Oct. 1977	2	39	31–48	56	19–94	0	—
		Apr. 1978	1	182	—	66	—	28	—
		Jul. 1978	4	146	122–175	61	44–89	31	23–42
		Oct. 1978	4	100	46–148	59	49–67	12	3–20
		Mean		113		60		18	

TABLE 3. (cont'd.). *Monthly mean whole-body insecticide levels in seven species of Des Moines River fish, 1977–78*

Species	Station	Date	Number of Analyses [1]	Residues, µg/kg Wet Weight					
				Dieldrin		ΣDDT		Heptachlor Epoxide	
				Mean	Range	Mean	Range	Mean	Range
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	3	47	13–71	220	89–329	7	2–6
		Jul. 1978	2	25	7–44	36	27–46	6	2–11
		Oct. 1978	5	26	8–50	39	29–63	1	0–3
		Mean		32		93		4	
Carp	1	Oct. 1977	4	47	43–51	64	39–101	1	0–2
		Apr. 1978	3	48	31–62	38	18–62	4	3–4
		Jul. 1978	4	47	42–51	32	15–70	13	8–23
		Oct. 1978	6	26	14–40	29	12–56	2	0–4
		Mean		40		43		5	
	2	Oct. 1977	3	19	13–27	18	14–25	0	—
		Apr. 1978	4	34	23–52	46	22–78	9	5–13
		Jul. 1978	2	46	34–59	35	21–49	9	7–11
		Oct. 1978	4	29	19–51	61	35–125	1	0–3
		Mean		31		43		4	
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	3	24	13–31	31	20–43	7	3–14
		Jul. 1978	3	47	39–59	50	45–57	11	7–14
		Oct. 1978	3	32	23–39	60	42–85	3	2–4
		Mean		35		47		7	
Channel catfish	1	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	3	59	31–98	29	22–37	12	6–22
		Oct. 1978	2	79	73–85	132	129–136	8	7–9
		Mean		67		70		10	
	2	Oct. 1977	3	71	69–74	25	16–40	0	—
		Apr. 1978	3	158	115–240	79	53–109	19	9–25
		Jul. 1978	3	192	180–215	90	73–118	40	37–42
		Oct. 1978	2	120	73–168	51	42–61	14	9–19
		Mean		136		62		18	
	3		1	101	—	101	—	10	—
White crappie	1	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	2	53	50–56	49	47–51	7	6–8
		Oct. 1978	1	29	—	59	—	1	—
		Mean		45		52		5	
	2	Oct. 1977	4	39	15–63	17	6–35	0	—
		Apr. 1978	1	21	—	37	—	5	—
		Jul. 1978	4	58	38–79	47	38–53	7	3–11
		Oct. 1978	1	88	—	71	—	6	—
		Mean		50		36		4	
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	4	94	31–301	49	28–60	8	4–19
		Jul. 1978	4	55	24–100	44	40–54	10	4–18
		Oct. 1978	2	63	63–64	63	54–72	5	4–6
		Mean		76		50		8	
Walleye	1	Oct. 1977	1	11	—	100	—	0	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	3	31	12–44	101	70–138	3	1–5
		Oct. 1978	2	15	14–17	119	119–120	0	—
		Mean		22		107		1	
	2	Oct. 1977	2	20	7–34	8	7–10	0	—
		Apr. 1978	1	42	—	30	—	5	—
		Jul. 1978	1	62	—	55	—	6	—
		Oct. 1978	0	—	—	—	—	—	—
		Mean		36		25		3	
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	1	33	—	92	—	2	—
		Oct. 1978	0	—	—	—	—	—	—
		Mean		33		92		2	
Largemouth bass	1	Oct. 1977	1	50	—	84	—	2	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	3	43	31–66	64	36–90	8	6–12
		Oct. 1978	5	81	22–182	82	60–109	7	0–23
		Mean		65		76		7	

TABLE 3. (cont'd.). *Monthly mean whole-body insecticide levels in seven species of Des Moines River fish, 1977–78*

Species	Station	Date	Number of Analyses [1]	Residues, µg/kg Wet Weight					
				Dieldrin		ΣDDT		Heptachlor Epoxide	
				Mean	Range	Mean	Range	Mean	Range
	2	Oct. 1977	3	37	15–50	14	7–20	0	—
		Apr. 1978	2	73	22–124	55	32–80	12	6–18
		Jul. 1978	5	50	22–90	69	50–93	8	4–10
		Oct. 1978	4	65	21–125	70	31–90	7	1–11
		Mean		55		55		6	
	3	Oct. 1977	0	—	—	—	—	—	—
		Apr. 1978	0	—	—	—	—	—	—
		Jul. 1978	1	49	—	72	—	9	—
		Oct. 1978	0	—	—	—	—	—	—
		Mean		49		72		9	

[1] Number of fish pooled for each analysis can be estimated by dividing total fish caught for that species on the collecting date and station given in Table 1 by number of analyses run.

collection date, spatial and temporal trends of pesticide levels in these species were difficult to determine and were examined selectively. Data from Station 2 that were suitable for checking seasonal trends in pesticide concentration revealed no consistent seasonal trend in dieldrin concentrations among these four species. Concentrations of dieldrin were highest in gizzard shad and white crappies in October 1978 and in channel catfish and walleyes in July. Available data revealed no statistically significant difference in dieldrin levels in the four species above, in, or below the reservoir.

More detailed data were available for river carpsuckers and carp. Dieldrin levels in individual samples of river carpsuckers ranged from 7 to 197 ppb; the mean was 63 ppb (Table 3). Again, no consistent seasonal trend was observed among fish from the three stations, and differences with respect to time of year were not statistically significant. Although dissolved dieldrin concentrations in water samples were similar at all three stations, carpsuckers collected in the reservoir during 1978 contained significantly higher dieldrin concentrations than did those collected above or below the reservoir during the corresponding sampling period ($F = 11.3$, $P = 0.001$).

Dieldrin concentrations in carp ranged from 13 to 62 ppb; mean was 36 ppb (Table 3). Seasonal differences in dieldrin concentration in carp were significant ($F = 5.79$, $P = 0.01$). Dieldrin concentrations were nearly constant in carp collected at Station 1 in October 1977 and April and July 1978 and had decreased in October 1978; the concentrations in carp collected at Stations 2 and 3 were highest in July. No consistent spatial trend was found among sampling dates. Mean dieldrin concentrations in carp collected at Stations 1, 2, and 3 were not significantly different throughout the sampling period.

Because dieldrin concentration in largemouth bass was related significantly to fish length, authors did not consider length when examining spatial and seasonal trends. Residues obtained by determining the difference between measured dieldrin concentration and calculated concentration, based on the regression formula of body length versus dieldrin (dieldrin [ppb] = 44.01 + 0.43 total body length [mm]), were used to compare stations. Largemouth bass of similar length, captured above and within the reservoirs, had similar concentrations of dieldrin. The single sample from below the reservoir was insufficient for comparison. Data on fish from Station 2 suggested that dieldrin concentrations in bass of similar length were highest in April, but the differences among sampling dates were not statistically significant.

No consistent seasonal trend for combined DDT–DDE–TDE (ΣDDT) levels was evident for any species of fish examined (Table 3). Greatest mean values occurred in October 1978 for five species and in April 1978 for the other two. At Station 2 (in the reservoir), where data were most nearly complete, concentrations were greatest in April in gizzard shad and river carpsuckers; in October 1978 in carp, crappies, and bass; and in July in channel catfish and walleye. Differences among stations were also not statistically significant. Mean concentrations in all species were greater in fish captured below the reservoir than in fish captured in the reservoir. In five species, mean concentrations in reservoir fish were either lower or equal to those found in fish collected above the reservoir.

Heptachlor epoxide occurred at lower levels than did dieldrin and ΣDDT in all species (Table 3). Concentrations were usually greatest in fish collected during July 1978. No distinct and consistent spatial trend was observed among species, except in river carpsuckers.

Heptachlor epoxide levels in 1978 were significantly higher in river carpsuckers collected in the reservoir than in those collected either above or below it ($F = 20.39$, $P = 0.0001$).

Discussion

The lack of measurable amounts of atrazine, alachlor, or cyanazine in fish tissue, even though significant concentrations of these compounds were usually present in the surrounding water, agreed with reports of rapid elimination of herbicides by exposed fish, with little or no accumulation of the compounds in body tissue (*2, 3, 9, 10*).

Not only did reservoir-captured fish other than river carpsucker fail to contain greater concentrations of insecticide than did fish captured above or below the reservoir, but fish collected where total insecticide concentrations in water were greatest also did not contain greater levels than fish collected elsewhere. Total concentrations of dieldrin in the river water above the reservoir were significantly higher than those within and below the reservoir (*6*), but concentrations in the fish collected from those locations did not reflect this spatial difference. A possible reason is that they absorbed only dieldrin in the dissolved state. Average concentrations of dieldrin detected in the aqueous phase of the river water were similar at all three locations over the study period (Table 2). Higher concentrations of dieldrin detected above the reservoir were due to the portion that was adsorbed onto the suspended sediment of the water. This adsorbed portion would probably be less available to fish. Another possibility is that the insecticide concentrations in the river water were so low at all three stations that fish were capable of metabolizing and eliminating the compounds as fast as they were absorbed and thus showed no difference in trace amounts left in the body.

Another possible explanation for lack of difference in pesticide concentrations in fish above, in, and below the reservoir may have been the newness of the reservoir and the short retention time for water. The reservoir was impounded in April 1977; consequently, the study period covered most of the first year of impoundment. Leung (*6*) estimated that 16 kg of dieldrin and 20 kg of *p,p'*-DDE were deposited in the reservoir between September 1977 and October 1978. Perhaps these amounts were too small to be recycled in sufficient quantity from sediment and accumulated by the fish through the food chain, if in fact bioaccumulation occurs in the reservoir. The potential for recycling pesticides from bottom sediment exists because dieldrin was present in all samples of Saylorville Reservoir bottom sediment analyzed during the study and ranged from 0.6 to 12.0 μg/kg (*6*). *ΣDDT* was present in some form in most samples and ranged from 0.0 to 17.1 μg/kg. Heptachlor epoxide was detected in four of 42 bottom samples collected and never exceeded 2.0 μg/kg. Also, water passed through the reservoir in fewer than 40 days during most of the study period because the reservoir was not full. The short retention time might also have affected movement of the deposited pesticide through the food chain by inhibiting buildup of phytoplankton and zooplankton populations. The effect of retention time in the reservoir on pesticide dynamics is not well known and would require further study. Also, inasmuch as this investigation covered only the first year of impoundment and deposition of pesticide-laden sediment, the occurrence and distribution of pesticides should be re-examined after several years of reservoir aging.

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Polychlorinated Biphenyls in Clams and Oysters from New Bedford Harbor, Massachusetts, March 1978 [1]

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ABSTRACT

Polychlorinated biphenyl (PCB) concentrations in clams (Mercenaria mercenaria) *and oysters* (Crassostrea virginica) *from 17 stations of the western and New Bedford Harbor areas of Buzzards Bay, Massachusetts, clearly show that the New Bedford Harbor area is severely polluted. Up to 5 ppm PCBs (dry weight) were found in shellfish tissue. The most likely sources of the PCBs are chronic releases from two electrical component manufacturers in New Bedford. Close proximity of the shellfish to the source of input is indicated by a high relative abundance of the di-, tri-, and tetrachlorobiphenyls. The data suggest that the New Bedford Harbor area should be considered, along with the Hudson River and Chesapeake Bay, one of the major sources of PCB inputs to the northeastern United States coastal area.*

Introduction

Following Jensen's report identifying polychlorinated biphenyls (PCBs) in organisms inhabiting Swedish waters (*10*), there emerged with each succeeding year further evidence of worldwide contamination (*15*). Although the U.S. Toxic Substances Control Act (1976) restricts further contamination, the toxicity of these compounds in conjunction with their resistance to environmental degradation (*7*) requires examination of their proximate and long-term effects on marine life. Their distribution and movement through the environment must be continuously monitored. Of particular concern are coastal areas where commercial and recreational shellfishing and fishing in benthic environments known to possess hazardous levels of PCBs may result in human consumption of contaminated organisms.

The presence of two large electrical component manufacturers, which use and discharge PCBs, combined with the existence of a local fishery suggested the importance of studying the distribution and accumulation of PCBs in the New Bedford, Massachusetts, area. This study used edible clams *(Mercenaria mercenaria* L.) and oysters *(Crassostrea virginica)* as indicators for several reasons: They are sessile and thus indicative of regional PCB distribution; they inhabit the benthic sediments in which large quantities of PCBs have been identified; they are microphagous and selectively process particles of the size range that adsorb PCBs (*3*; private communication: B. Dangle. 1978. U.S. Environmental Protection Agency, Toxic Substances Pesticides Branch, Air and Hazardous Material Division, Boston, Mass.); and they are significant in local sport and commercial fisheries.

Materials and Methods

COLLECTION OF SPECIES

Clams ranging in size from 37 to 106 mm were obtained with an epibenthic sled at depths varying from 3 to 12 meters. The majority of sampling sites were located in Buzzards Bay within a 5.8-nautical-mile radius of the entrance to New Bedford Harbor (Figure 1). For comparison, additional specimens were collected from the Westport River, 1.0 nautical miles from its mouth and 14.0 nautical miles from New Bedford Harbor. These organisms served as low-level control samples. The precise locations of sampling sites within the study area were determined largely by the distribution of the organisms. The Slocum River estuary was also sampled. Because *M. mercenaria* was not available, authors collected *Crassostrea virginica* (Gmelin) as the representative bivalve for this area.

All sampling was conducted during the week of March 11, 1978. Thus, the reported effects of water temperature on PCB concentrations (*4*) were obviated. Bottom characteristics of collection sites ranged from soft mud to unsorted sand densely infiltrated with shell debris.

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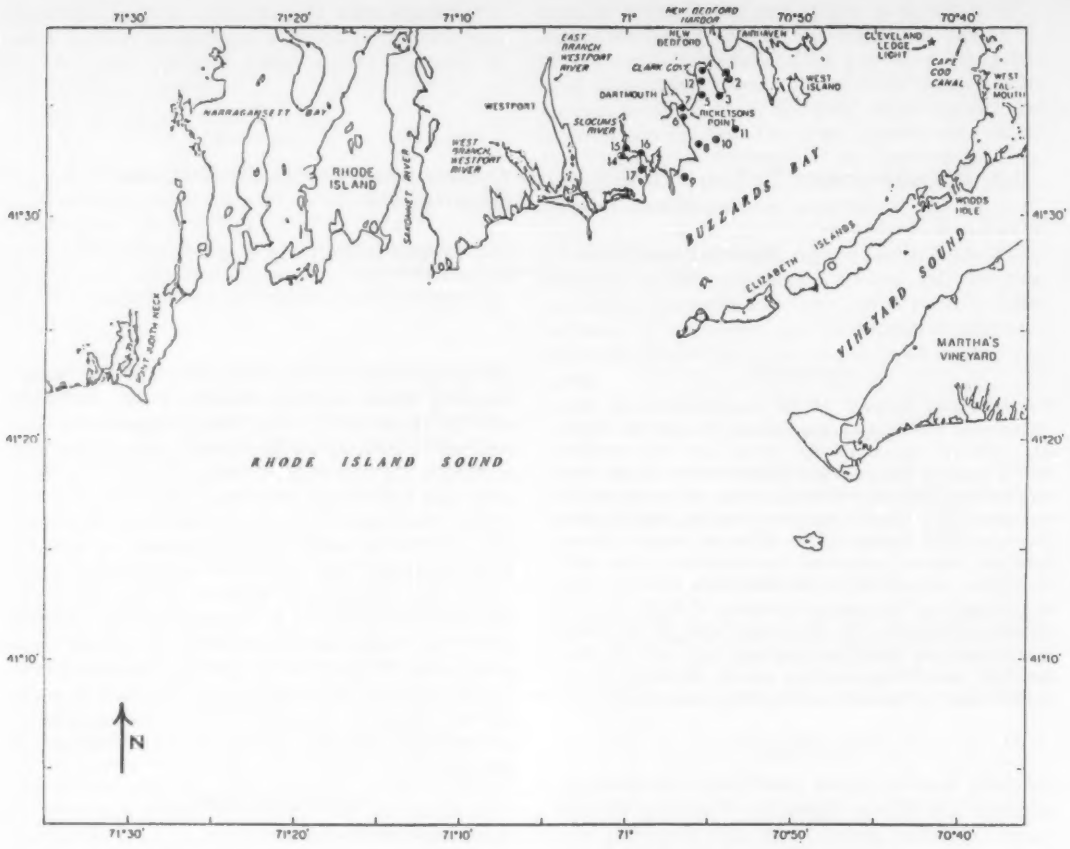

FIGURE 1. *Sites along Buzzards Bay for the sampling of shellfish contaminated with PCBs.*

ANALYTICAL METHODS

PCBs were quantitatively determined in pooled tissue homogenates. All chromatographic reagents, glassware, and equipment contacting the samples were copiously rinsed with reagent grade, redistilled solvents (Fisher Scientific Co.), in the following sequence: methanol, acetone, toluene, and hexane.

The shucked clams including mantle cavity water were homogenized (Polytron R. Kinematica GmbH), lyophilized, and extracted three times with hexane—one 50-ml portion and two 25-ml portions. The extracts were filtered through a column of powdered sodium sulfate (Na_2SO_4) to remove residual water and particulates and then concentrated to 1 ml for column chromatographic cleanup. The cleanup columns were packed with 10 g of 200-mesh alumina and 8 g of 60–200-mesh silica gel, both deactivated 5% with water. The columns were first eluted with 15 ml hexane. PCBs were then collected in a 50-ml hexane–toluene (80 + 20) elution and quantitatively concentrated for gas-liquid chromatographic (GLC) analysis. GLC instrument parameters and operating conditions were as follows:

Chromatograph:	Hewlett-Packard, 7620A
Detector:	^{63}Ni electron-capture
Column:	glass, 6-ft long by 2-mm ID, packed with a mixture of 1.5% OV-17 and 1.95% QF-1 on 100–200-mesh Chromosorb W(AW)
Temperatures:	injection port 225°C oven, isothermal 190°C detector 300°C
Pulse interval:	50 mseconds
Carrier gas:	a mixture of 95% argon and 5% methane flowing at 20 ml/min
Detector purge:	40 ml/min
Chart speed:	0.5 inches/min

PCBs were quantitated by comparing the summation of eight individual peak areas with a separately injected Aroclor 1254 or 1242 standard. The limit of detection,

based on the studies of shellfish by Goldberg et al. (*6*), was 0.001 ppm dry weight. Recovery of PCBs from samples spiked with Aroclor 1254 before extraction was 80%–90% or better. PCBs were confirmed by glass capillary gas chromatographic/mass spectrometric (GCMS) analyses at the Woods Hole Oceanographic Institution Laboratory using a Finnigan Model 1015 SL system modified for glass capillary GC.

Results

PCBs reported as Aroclor 1254 were detected in all samples, ranging from 4.19 ppm dry weight in samples collected adjacent to the harbor down to 0.232 ppm in samples collected approximately 3 nautical miles from the harbor (Table 1). Samples from Westport Harbor, Massachusetts (Site 13), containing 0.008 ppm PCB were considered indicative of background concentrations.

TABLE 1. *Aroclor 1254 concentrations in* Mercenaria mercenaria *and* Crassostrea virginica, *1978*

Sampling Site	Av. Concn × 10^{-6} g/g Dry Wt [1]	Av. Concn × 10^{-6} g/g Wet Wt	Av. Concn Corrected for 80% Extn Efficiency, × 10^{-6} g/g Dry Wt
	Mercenaria mercenaria		
1	4.19	0.524	5.24
2	1.36	0.170	1.70
3	1.75	0.218	2.19
4	0.443	0.055	0.553
5	1.54	0.192	1.92
6	1.42	0.177	1.77
7	0.290	0.036	0.362
8	0.625	0.078	0.781
9	0.537	0.067	0.671
10	0.232	0.029	0.290
11	1.04	0.130	1.30
12	0.879	0.110	1.10
13	0.008	0.001	0.010
	Crassostrea virginica		
14	0.560	0.070	0.700
15	2.57	0.321	3.21
16	2.28	0.284	2.84
17	1.47	0.184	1.84

[1] Samples were analyzed at Southeastern Massachusetts University Laboratories.

Examination of the data suggests a gradient of decreasing concentration from point-source contamination similar in pattern to that reported from the upper Hudson River (*1*). The lower concentrations found in protected coves and estuaries indicate minimal PCB input from urban runoff.

The Commonwealth of Massachusetts has prohibited commercial fishing north of a line drawn from Ricketson's Point, Dartmouth (41°34′38″N; 70°56′19″W), to Black Rock, Fairhaven (41°34′41″N; 70°51′45″W). Sampling sites south of this closed fishing area, however, showed PCB concentrations comparable to those within the restricted area. High PCB concentrations at Sites 6 and 8 may be due to transport paralleling the mass flow of water in Buzzards Bay (*14*). The elevated PCB concentration of Site 11 may be due to tidal flushing along the major shipping channel away from the harbor.

A few samples were analyzed in more detail in the Woods Hole Oceanographic Institution Laboratory. These analyses showed that the PCBs were composed of a mixture of components similar to Aroclor 1242 or 1016 and 1254. In addition, authors analyzed a sample of scallops (*Aequipecten irradians* Lamarck) from Cleveland Ledge Light (Figure 1) supplied by the Falmouth, Massachusetts, shellfish warden. The data from these analyses are presented in Table 2.

TABLE 2. *Mixture of Aroclors 1242 and 1254 in selected samples from New Bedford Harbor and Buzzards Bay, Massachusetts, 1978*

Site	Organism	Residues × 10^{-6} g/g Dry Wt [1] 1242	1254
3	*Mercenaria mercenaria*	1.59	1.46
10	*Mercenaria mercenaria*	0.22	0.20
Cleveland Ledge	*Aequipecten irradians*	0.093	0.185

[1] Samples were analyzed at Woods Hole Oceanographic Institute.

Discussion

In compliance with the U.S. Toxic Substance Control Act, the manufacturing facilities abutting New Bedford Harbor have severely curtailed the discharge of PCBs into harbor waters. All PCB use was, in fact, suspended as of September 1978 (Private Communications: Anonymous. 1978. Aerovox Inc. spokesperson; Robinson, W. 1978. Cornell Dubilier, Inc., spokesperson, both of New Bedford, Mass.).

However, the discharge of large amounts of PCBs over the last 38 years, coupled with the affinity of PCBs for sediments (*8*), has resulted in severely contaminated sediments in this area. The literature reveals little data for PCBs in sediments from this area. Harvey and Steinhauer (*9*) reported 8.4 x 10^{-6} g PCB/g dry weight in outer New Bedford Harbor sediment samples in 1973. Gilbert et al. (*5*), reported values of 0.175–0.543 x 10^{-6} g/g dry weight for concentrations of PCBs in surface sediments from eight stations in Buzzards Bay outside New Bedford Harbor.

deLappe and Risebrough (*3*) analyzed mussels (*Mytilus edulis* L.) from inner New Bedford Harbor and re-

ported a phenomenally high concentration of 110 x 10^{-6} g PCB/g dry weight. They also analyzed water from the area and found concentrations up to 580 x 10^{-9} g PCB/liter of dissolved and particulates combined.

Samples of shellfish, bottom fish, and sediments from the New Bedford Harbor area were analyzed in 1976 and 1977 for PCBs. Concentration ranged as follows: 0.5–620 x 10^{-6} g PCBs/dry weight sediments; up to 11.7 x 10^{-6} g PCBs/g wet weight of lobster (*Homarus americanus* Milne-Edwards) edible tissue; and up to 20.0 x 10^{-6} g PCBs/g wet weight black back flounder (*Pseudopleuronectes americanus*, Walbaum) edible tissue (unpublished data: Commonwealth of Massachusetts, Department of Environmental Quality Engineering, 1976–77). These data led to the closure of the New Bedford Harbor area as previously noted.

Summerhayes et al. (*14*) and Stoffers et al. (*12*) investigated trace metal contamination of New Bedford Harbor sediments. They found up to 1% Cu in surface sediments in the inner harbor and concluded that the harbor area was slowly leaking trace metal-contaminated sediments to nearby Buzzards Bay. Processes active in movement of trace metal-contaminated sediments are likely to be active in the movement of PCBs in the same sediments.

Thus, even though PCB discharges by industry have been curtailed, harbor sediments contain high concentrations of PCBs and can act as a source of PCB contamination of the harbor for some time to come. Young et al. (*16*) clearly demonstrated that PCB-contaminated sediments can be a source of PCB contamination for shellfish. Rhoads (*11*) showed that tidal influences in Buzzards Bay result in resuspension of surface sediments in some areas with the resulting probability of transport to other areas of the bay. Disturbance of the sediments in New Bedford Harbor by natural events such as tidal movement or storms or by man-induced activities such as dredging will probably result in contamination of other Buzzards Bay areas.

This may be the reason PCBs were detected in the bay sediments by Gilbert et al. (*5*) and in scallops at Cleveland Ledge Light in the present study. However, PCBs are so ubiquitous in coastal regions near industrialized areas that authors cannot be certain at present of the origin of the low concentrations of PCBs at Cleveland Ledge Light and Buzzards Bay surface sediments.

Data on PCBs in New Bedford Harbor are sufficient to identify this area as one of high PCB concentration in both sediments and biota. However, the exact magnitude of the problem has not yet been investigated. Critical questions of the size of the reservoir of PCBs in the sediments of the harbor and the extent to which they are a source for contamination of other areas of Buzzards Bay remain and are being pursued.

The few higher-resolution measurements available to us at this time indicate that there is a substantial concentration of the di, tri- and tetrachlorobiphenyls in the area compared with the amounts of penta- and hexachlorobiphenyls usually found in environmental samples. This indicates a proximity of the samples analyzed to source of input via effluents. The di- and trichlorobiphenyls are more reactive than the penta- and hexachlorobiphenyls and, as distance and time between input and measurement increase, there is a greater probability that the less-chlorinated biphenyls will undergo reaction (*15*). The electrical component manufacturers in New Bedford used primarily Aroclor 1242 and 1016 mixtures. Thus, the input of the less-chlorinated analogs is expected. The New Bedford Harbor and Buzzards Bay ecosystems provide a system to study the biogeochemistry of the various PCB isomers and authors are currently pursuing this investigation.

Our data on the PCBs in oysters from the Slocum River estuary (Table 1) may suggest a second problem with PCBs in the greater New Bedford area. PCB concentrations in *C. virginica* from the Slocum River estuary are in excess of those in *M. mercenaria* collected off the river mouth. It is possible that lateral transport of contaminated sediments from the New Bedford Harbor area to a point upstream in the adjacent Slocum River would exceed transport to a point off the mouth of the river. This is unlikely but cannot be ascertained because of lack of knowledge about sediment transport in the area. A second possibility is the release of PCBs from a landfill site to the aquifer feeding the Slocum River. It has been established that there are over 200,000 kg of PCBs buried in the New Bedford municipal landfill located on the aquifer feeding the Slocum River valley. A few preliminary measurements have shown that some PCBs are present in waters draining from the landfill (*13*). Extensive contamination of groundwaters was not found, based on a few measurements. However, time series measurements and mass flow calculations have not been made (*13*). This problem merits more extensive study because the aquifer represents the primary source of drinking water for the town of Dartmouth, Massachusetts.

Recent measurements of PCBs in the common blue mussel *(Mytilus edulis)* and in oysters *(Crassostrea virginica)* collected around the coast of the United States have shown that the northeastern U.S. coastal area is more contaminated with PCBs on a regional

basis than most other areas of the coast (*6*). The data and discussions presented here suggest that the New Bedford Harbor area should be considered along with the Hudson River and Chesapeake Bay as one of the sources of these regionally elevated concentrations.

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Nationwide Residues of Organochlorine Compounds in Wings of Adult Mallards and Black Ducks, 1979–80

Brian W. Cain [1]

ABSTRACT

Organochlorine residues in wings of adult mallards (Anas platyrhynchos) *and black ducks* (Anas rubripes) *were monitored nationwide from birds harvested during the 1979–80 hunting season. DDE residues were found in all samples. DDT residues had declined from levels reported in 1976 on a flyway basis but the decline was significant ($P < 0.05$) only in the Pacific Flyway. Levels of DDT, DDE, TDE, and dieldrin were low on a flyway basis, and all but DDE declined significantly ($P < 0.05$) in the percent occurrence. Polychlorinated biphenyls (PCB) levels were lower in mallard wings from all flyways compared with 1976 data, but percent occurrence had significantly ($P < 0.05$) increased. Pools from Alabama and New Mexico continued to show higher DDE residues than pools from other areas.*

Introduction

During the 1965–66 hunting season, the Fish and Wildlife Service, U.S. Department of the Interior, as part of the National Pesticide Monitoring Program (*2*), began to monitor organochlorine pesticides in duck wings collected by hunters. Justification for this method of collection was given by Johnson et al. (*5*). The black duck ranges over a large part of the Atlantic Flyway and the mallard is found throughout the rest of the contiguous 48 states. Thousands of wings collected each year by cooperating hunters are sent to collection sites in each of the four flyways. Waterfowl migrate twice a year within four major flyways that consist of states or parts of states in which the birds feed or rest for short periods of time. Millions of waterfowl spend the winter months in the southern portions of these flyways, and may be exposed to environmental contaminants different from those found in northern nesting areas.

Heath and Prouty (*4*) successfully tested the monitoring methodology in 1965 using mallard and black duck wings collected from New York and Pennsylvania. A later report showed there was a highly significant correlation between DDT residues in the wing and those in breast skin, breast muscle, brain, kidney, liver, and other tissues from captive mallards and scaup ducks (*1*).

This paper presents results from the mallard and black duck wings collected during the 1979–80 hunting season and includes the mean residue levels for each state. The percentage of the pools from each flyway that contain a particular contaminant residue is presented and compared with the 1976-77 hunting season. The mean value of organochlorine residues in wings by major flyways is presented and compared with the 1976 collection.

Methods

WING COLLECTIONS

During the 1979-80 hunting season, cooperating waterfowl hunters mailed approximately 11,660 wings from adult mallards or black ducks to a regional collection point within each of the four flyways. Each wing was sent in a separate envelope that listed the date, county, and state where the bird was harvested. The wings were held in frozen storage until March or early April 1980 when biologists determined the sex and maturity of each bird. Only adult wings were used for the pesticide monitoring program to maintain the sampling consistency established by Heath and Hill (*3*). Wings from each state were sorted randomly into pools of 25 wings, and random samples of these pools were made by using a random numbers table. The number of pools taken was such that about 50% of the wings submitted from a state were selected for organochlorine analyses. Each pool of 25 wings was wrapped in aluminum foil, tagged with a coded number, frozen, and shipped to Raltech Scientific Services, Inc. (formerly WARF Institute, Inc.) in Madison, Wisconsin. There were 24 pools of black duck wings and 29 pools of mallard wings from the Atlantic Flyway, 64 pools of mallard wings from the Mississippi Flyway, 54 pools of mallard wings from the Central Flyway, and 44 pools of mallard wings from the Pacific Flyway.

[1] Fish and Wildlife Service, U.S. Department of the Interior, Patuxent Wildlife Research Center, Laurel, MD 20811

ANALYTICAL PROCEDURES

Wings in each pool were trimmed by removing most of the feathers and the distal joint with a pair of scissors. Remaining portions were homogenized in a Hobart grinder, and approximately 10 g was removed, weighed, and placed in a preweighed 150-ml beaker. The beaker and sample were oven-dried 2 weeks at 40°C and reweighed, and the sample dry weight was recorded. Approximately 40 g homogenized sample was weighed into a 250-ml beaker and mixed with 100 g anhydrous sodium sulfate, placed overnight in a hood, and then transferred to a 43-mm by 123-mm prewashed Whatman extraction thimble plugged with glass wool. The thimble was placed in a desiccator overnight and then extracted for 8 hours in a Soxhlet apparatus with a mixture of 150 ml each of ethyl ether and petroleum ether. This solution was then concentrated on a steam bath, and the residue was transferred to a 50-ml volumetric flask and diluted to volume with a mixture of dichloromethane–cyclohexane (15 + 85).

A 5-ml aliquot of the extract was placed in an Auto-Prep 1001 gel permeation chromatograph that had been standardized for chlorinated insecticides and PCB compounds. The column was glass, 600 mm by 25 mm, and packed with 60 g of 200–400-mesh Bio-Beads (SX-3). The solvent was dichloromethane–cyclohexane (15 + 85) at the flow rate of 5.5 ml/min. The resulting solution was concentrated on a flash evaporator to approximately 1 ml in the presence of 5 ml iso-octane and diluted to 25 ml with petroleum ether. A 10-ml aliquot of this gel permeation extract was placed in a 25-g silica-gel 60 column and three elutions were prepared. The first was eluted with 90 ml petroleum ether and contained hexachlorobenzene (HCB) and mirex; the second was eluted with 200 ml petroleum ether and contained PCB compounds and DDE; and the third was eluted with 150 ml of a mixture of acetonitrile–hexane–dichloromethane (1 + 19 + 80) and contained the remaining chlorinated insecticides. Fraction three was concentrated on a flash evaporator to 1 ml and diluted to 10 ml with petroleum ether. Four microliters from each fraction was injected into a gas chromatograph equipped with an electron-capture detector.

Instrument parameters and operating conditions applied to all samples except where differences are noted:

Column:	2 m by 4 mm
Packings:	(1) organochlorine pesticides and PCBs: a mixture of 1.95% OV-17 and 1.5% QF-1 on 100–200-mesh Supelcoport (2) chlordane isomers: 3% OV-1 on 80–100-mesh Gas-Chrom Q
Temperatures, °C	column 200 injector 250 detector 300
Carrier gases:	a mixture of 95% argon and 5% methane
Flow rates	(1) 33 ml/min (2) 32 ml/min

Lipids were determined by using a 5-ml aliquot of the Soxhlet extract in a preweighed 2-dram vial. The vial was placed in a 40°C oven for 3 days to remove the solvent and then reweighed, and the amount of the lipids was calculated.

All residues are expressed as ppm wet weight and may be converted to an approximate dry or lipid weight by dividing by 0.60 or 0.14, the mean proportions of dry or lipid material in the samples, respectively. Mean residue values were calculated by using 0.00 as the value for samples in which no residue was reported at the 0.01-ppm sensitivity level. The recovery percentages from spiked samples were DDE, 85; TDE, 125; dieldrin, 98; heptachlor epoxide, 90; and Aroclor 1254, 118. Analytical results have not been corrected for recovery. Residues in 5% of the pools were confirmed by mass spectrometry.

The percentage occurrence of the organochlorines in wings from each flyway were compared with the 1976 collection data by using a test for two population proportions. Mean residue levels of DDE, DDT, TDE, dieldrin, and PCBs were compared on a flyway basis with the published 1976 data of White (*8*) by using only those samples with a detectable residue level. A *t*-test comparison was made on each data pair that had detectable residues in at least 50% of the pools collected. A $P < 0.05$ was necessary for significance for all statistical comparisons.

Results and Discussion

Residues of DDE, DDT, TDE, dieldrin, and PCBs in the duck wings from the 1979–80 hunting season are presented in Table 1. These data, collected from 5,268 wings (215 pools), are presented as mean values for each state in a flyway and are arranged in a North to South direction. Data in Table 1 should not be interpreted on a statewide basis alone because waterfowl migrate and may cover a wide area and range of habitats in many states. Samples from some localities (i.e., Alabama and New Mexico) continue to show higher residues of DDT and DDE than do samples from the other localities. This situation in Alabama was reported earlier (*3, 7, 8*), and a possible source of the contamination was described by O'Shea et al. (*6*).

The highest DDE level, 3.28 ppm, was detected in a pool composed of wings from Arizona and New Mexico, and the lowest level of DDE residue, 0.02 ppm, occurred in pools from Florida and Kentucky. DDE residues occurred in all wing pools; however, DDT, TDE, and dieldrin were found in fewer pools in the 1979–80 wing collection than in the 1976–77 collection

TABLE 1. *Organochlorine residues in pools of wings from adult mallards and black ducks, 1979–80*

State	Number of Pools	Residues, ppm Wet Weight									
		DDE		DDT		TDE		Dieldrin		PCBs	
		$\bar{x} \pm SE$	Range	$\bar{x} \pm SE$	Range	$\bar{x} \pm SE$	Range	$\bar{x} \pm SE$	Range	$\bar{x} \pm SE$	Range
BLACK DUCKS, ATLANTIC FLYWAY											
Maine	2	0.13 ± 0.00 (2)	0.12–0.15	ND		ND		ND		0.21 ± 0.00 (2)	0.19–0.23
Vermont	1[1]	0.12 ± 0.00	—	ND		ND		ND		0.42 ± 0.00	—
New Hampshire	1[1]	0.42 ± 0.00	—	0.01 ± 0.00	—	ND		ND		0.74 ± 0.00	—
Massachusetts	2	0.54 ± 0.07 (2)	0.47–0.60	0.03 ± 0.01 (2)	0.02–0.03	0.11 ± 0.09 (2)	0.02–0.20	0.09 ± 0.06 (2)	0.03–0.14	0.87 ± 0.03 (2)	0.84–0.89
Connecticut	1	0.08 ± 0.00	—	0.02 ± 0.00	—	ND		0.01 ± 0.00	—	1.49 ± 0.00	—
Rhode Island	2[1]	0.47 ± 0.11 (2)	0.36–0.58	0.03 ± 0.01 (2)	0.02–0.03	0.02 ± 0.01 (2)	0.01–0.02	0.03 ± 0.01 (2)	0.02–0.03	0.84 ± 0.25 (2)	0.59–1.09
New York	2	0.44 ± 0.22 (2)	0.22–0.66	0.02 ± 0.00 (1)	ND–0.02	0.02 ± 0.00 (1)	ND–0.02	0.02 ± 0.00 (2)	0.02–0.02	1.31 ± 0.25 (2)	0.82–1.80
Pennsylvania	1	0.11 ± 0.00	—	ND		ND		ND		0.49 ± 0.00	—
New Jersey	3	0.53 ± 0.09 (3)	0.37–0.68	0.01 ± 0.01 (2)	ND–0.02	0.01 ± 0.01 (2)	ND–0.02	0.01 ± 0.00 (2)	0.01–0.02	0.55 ± 0.01 (3)	0.54–0.56
Delaware	1	0.67 ± 0.00	—	ND		ND		ND		0.80 ± 0.00	—
Maryland	2	0.22 ± 0.07 (2)	0.15–0.29	ND		ND		0.01 ± 0.00 (1)	ND–0.01	0.29 ± 0.04 (2)	0.25–0.33
Virginia	2	0.18 ± 0.02 (2)	0.16–0.19	ND		ND		ND		0.21 ± 0.02 (2)	0.19–0.22
West Virginia	1[1]	0.23 ± 0.00	—	ND		ND		0.01 ± 0.00	—	0.57 ± 0.01	—
North Carolina	1[1]	0.15 ± 0.00	—	ND		ND		ND		0.15 ± 0.00	—
South Carolina	1	0.37 ± 0.00	—	ND		ND		0.01 ± 0.00	—	1.00 ± 0.00	—
Georgia and Florida	1[1]	0.11 ± 0.00	—	ND		ND		ND		0.45 ± 0.00	—
MALLARDS, ATLANTIC FLYWAY											
Maine	1[1]	0.21 ± 0.00	—	0.02 ± 0.00	—	ND		ND		0.28 ± 0.00	—
Vermont	1[1]	0.09 ± 0.00	—	0.02 ± 0.00	—	ND		ND		0.14 ± 0.00	—
New Hampshire	1[1]	0.20 ± 0.00	—	0.01 ± 0.00	—	ND		ND		0.27 ± 0.00	—
Massachusetts	2	0.33 ± 0.12 (2)	0.21–0.45	0.02 ± 0.01 (2)	0.01–0.02	0.02 ± 0.00 (2)	0.02–0.02	0.05 ± 0.03 (2)	0.02–0.07	0.05 ± 0.03 (2)	0.02–0.07
Connecticut	1	0.14 ± 0.00	—	ND		ND		ND		1.17 ± 0.00	—
Rhode Island	1	0.58 ± 0.00	—	0.03 ± 0.00	—	0.01 ± 0.00	—	0.04 ± 0.00	—	0.98 ± 0.00	—
New York	2	0.48 ± 0.26 (2)	0.41–0.55	0.03 ± 0.00 (2)	0.03–0.03	ND		0.02 ± 0.00 (2)	0.02–0.02	0.79 ± 0.09 (2)	0.70–0.87
Pennsylvania	3	0.23 ± 0.02 (3)	0.20–0.28	0.01 ± 0.01 (2)	ND–0.02	ND		0.01 ± 0.00 (1)	ND–0.01	0.49 ± 0.15 (3)	0.28–0.77
New Jersey	2	0.47 ± 0.06 (2)	0.41–0.52	0.02 ± 0.01 (2)	0.01–0.02	0.01 ± 0.00 (2)	0.01–0.01	0.02 ± 0.01 (2)	0.01–0.02	0.55 ± 0.61 (2)	0.44–0.65
Delaware	2	0.57 ± 0.15 (2)	0.42–0.71	ND		ND		0.01 ± 0.00 (2)	0.01–0.01	0.41 ± 0.03 (2)	0.38–0.43
Maryland	2	0.12 ± 0.01 (2)	0.11–0.13	ND		ND		0.01 ± 0.00 (2)	0.01–0.01	0.21 ± 0.06 (2)	0.15–0.27
Virginia	3	0.15 ± 0.05 (3)	0.08–0.25	0.01 ± 0.00 (1)	ND–0.02	ND		0.01 ± 0.01 (1)	ND–0.01	0.29 ± 0.08 (3)	0.15–0.44
West Virginia	1[1]	0.23 ± 0.00	—	ND		ND		ND		0.38 ± 0.00	—
North Carolina	2	0.13 ± 0.03 (2)	0.10–0.15	ND		ND		0.02 ± 0.01 (2)	0.01–0.03	0.87 ± 0.75 (2)	0.12–1.62
South Carolina	2	0.15 ± 0.08 (2)	0.07–0.23	0.01 ± 0.01 (1)	ND–0.01	ND		0.28 ± 0.27 (2)	0.01–0.55	0.14 ± 0.08 (2)	0.06–0.21
Georgia	2	0.37 ± 0.20 (2)	0.17–0.57	ND		ND		0.01 ± 0.01 (1)	ND–0.01	0.12 ± 0.04 (2)	0.08–0.15
Florida	1[1]	0.02 ± 0.00	—	0.02 ± 0.00	—	ND		ND		0.09 ± 0.00	—

MALLARDS, MISSISSIPPI FLYWAY											
Minnesota	4	0.10 ± 0.03 (4)	0.04–0.15	0.00 ± 0.00 (1)	0.00–0.01		ND	0.00 ± 0.00 (1)	ND–0.01	0.08 ± 0.02 (4)	0.04–0.14
Wisconsin	5	0.10 ± 0.02 (5)	0.06–0.18		ND		ND		ND	0.12 ± 0.02 (5)	0.07–0.20
Michigan	5	0.16 ± 0.03 (5)	0.10–0.29		ND		ND	0.00 ±0.00 (2)	ND–0.01	0.20 ± 0.04 (5)	0.10–0.31
Iowa	6	0.09 ± 0.01 (6)	0.08–0.11		ND		ND	0.03 ± 0.02 (4)	ND–0.12	0.07 ± 0.03 (6)	0.02–0.20
Illinois	5	0.15 ± 0.05 (5)	0.06–0.34	0.000 ± 0.00 (1)	ND–0.02		ND	0.01 ± 0.00 (4)	ND–0.02	0.16 ±0.08 (5)	0.03–0.45
Indiana	3	0.26 ± 0.09 (3)	0.12–0.43	0.02 ± 0.02 (1)	ND–0.05	0.01 ± 0.00 (1)	ND–0.02	0.00 ± 0.00 (1)	ND–0.01	0.16 ± 0.05 (3)	0.08–0.25
Ohio	3	0.17 ± 0.02 (3)	0.12–0.20	0.00 ± 0.00 (1)	ND–0.01		ND	0.01 ± 0.01 (2)	ND–0.02	0.51 ± 0.09 (3)	0.35–0.64
Missouri	5	0.06 ± 0.02 5)	0.02–0.12		ND		ND	0.00 ± 0.00 (1)	ND–0.01	0.03 ± 0.01 (5)	0.01–0.06
Kentucky	2	0.09 ± 0.07 (2)	0.02–0.15		ND		ND	0.01 ±0.00 (2)	0.01–0.01	0.12 ± 0.06 (2)	0.06–0.18
Arkansas	7	0.15 ± 0.03 (7)	0.07–0.27	0.01 ± 0.00 (4)	ND–0.01		ND	0.01 ± 0.00 (7)	0.01–0.02	0.03 ± 0.01 (6)	ND–0.06
Tennessee	4	0.09 ± 0.02 (4)	0.04–0.12	0.00 ± 0.00 (1)	ND–0.01		ND	0.02 ± 0.01 (4)	0.01–0.03	0.07 ± 0.02 (4)	0.02–0.10
Louisiana	6	0.08 ± 0.01 (6)	0.05–0.12	0.00 ± 0.00 (1)	ND–0.01		ND	0.01 ± 0.00 (4)	ND–0.01	0.03 ± 0.00 (6)	0.02–0.04
Mississippi	5	0.21 ± 0.03 (5)	0.11–0.26	0.03 ± 0.01 (4)	ND–0.05	0.01 ± 0.01 (3)	ND–0.05	0.02 ± 0.00 (5)	0.01–0.03	0.04 ± 0.01 (5)	0.02–0.05
Alabama	4	0.85 ± 0.29 (4)	0.29–1.48	0.13 ± 0.03 (4)	0.09–0.21	0.09 ± 0.03 (4)	0.02–0.17	0.31 ± 0.29 (4)	0.01–1.18	0.14 ± 0.03 (4)	0.11–0.22
MALLARDS, CENTRAL FLYWAY											
Montana (eastern)	4	0.04 ± 0.01 (4)	0.04–0.10		ND		ND		ND	0.04 ± 0.01 (4)	0.02–0.07
North Dakota	6	0.05 ± 0.01 (6)	0.04–0.08	0.00 ± 0.00 (1)	ND–0.01		ND		ND	0.04 ± 0.02 (6)	0.02–0.12
South Dakota	4	0.08 ± 0.02 (4)	0.05–0.12	0.02 ± 0.01 (2)	ND–0.05		ND		ND	0.06 ± 0.04 (4)	0.04–0.10
Wyoming (eastern)	4	0.06 ± 0.02 (4)	0.04–0.11	0.01 ± 0.01 (1)	ND–0.02		ND	0.01 ± 0.01 (1)	ND–0.02	0.05 ± 0.01 (4)	0.03–0.07
Nebraska	8	0.06 ± 0.01 (8)	0.03–0.14		ND		ND	0.01 ± 0.01 (2)	ND–0.05	0.02 ± 0.01 (5)	ND–0.06
Colorado (eastern)	6	0.09 ± 0.02 (6)	0.04–0.18	0.01 ± 0.00 (4)	ND–0.02		ND	0.02 ± 0.00 (6)	0.01–0.02	0.12 ± 0.02 (6)	0.05–0.18
Kansas	5	0.04 ± 0.01 (5)	0.03–0.05		ND		ND		ND	0.01 ± 0.00 (3)	ND–0.02
New Mexico (eastern)	3	0.16 ± 0.05 (3)	0.06–0.24		ND		ND		ND	0.10 ± 0.02 (3)	0.05–0.14
Oklahoma	7	0.11 ± 0.18 (7)	0.04–0.17	0.00 ± 0.00 (1)	ND–0.01		ND	0.00 ± 0.00 (2)	ND–0.01	0.06 ± 0.01 (7)	0.03–0.11
Texas	7	0.28 ± 0.11 (7)	0.04–0.69	0.02 ± 0.02 (3)	ND–0.11	0.00 ± 0.00 (1)	ND–0.02	0.00 ± 0.00 (1)	ND–0.01	0.07 ± 0.02 (7)	0.02–0.14
MALLARDS, PACIFIC FLYWAY											
Washington State	9	0.24 ± 0.07 (9)	0.10–0.77	0.02 ± 0.01 (7)	ND–0.06	0.00 ± 0.00 (1)	ND–0.01	0.01 ± 0.00 (5)	ND–0.01	0.04 ± 0.00 (8)	ND–0.11
Oregon	4	0.57 ± 0.22 (4)	0.18–1.20	0.02 ± 0.01 (3)	ND–0.05		ND	0.00 ± 0.00 (1)	ND–0.01	0.08 ± 0.01 (4)	0.05–0.11
Idaho	8	0.28 ± 0.07 (8)	0.13–0.71	0.02 ± 0.01 (6)	ND–0.05		ND	0.00 ± 0.00 (2)	ND–0.01	0.06 ± 0.01 (8)	0.03–0.12
Montana (western)	5	0.05 ± 0.01 (5)	0.04–0.07		ND		ND		ND	0.02 ± 0.01 (4)	ND–0.04

TABLE 1. (cont'd.). *Organochlorine residues in pools of wings from adult mallards and black ducks, 1979–80*

State	Number of Pools	Residues, ppm Wet Weight									
		DDE		DDT		TDE		Dieldrin		PCBs	
		$\bar{x} \pm$ SE	Range	$\bar{x} \pm$ SE	Range	$\bar{x} \pm$ SE	Range	$\bar{x} \pm$ SE	Range	$\bar{x} \pm$ SE	Range
Wyoming (western)	2	0.08 ± 0.03 (2)	0.05–0.10	ND		ND		ND		0.01 ± 0.00 (1)	ND–0.02
California	6	0.34 ± 0.10 (6)	0.06–0.72	0.01 ± 0.00 (3)	ND–0.02	ND		0.01 ± 0.00 (3)	ND–0.02	0.05 ± 0.02 (6)	0.01–0.11
Nevada	2	0.12 ± 0.01 (2)	0.11–0.13	ND		ND		0.01 ± 0.01 (1)	ND–0.01	0.07 ± 0.01 (2)	0.06–0.07
Utah	2	0.31 ± 0.06 (2)	0.25–0.37	0.04 ± 0.03 (2)	0.01–0.06	ND		0.01 ± 0.01 (1)	ND–0.01	0.11 ± 0.07 (2)	0.04–0.18
Colorado (western)	3	0.60 ± 0.12 (3)	0.37–0.72	0.02 ± 0.01 (2)	ND–0.04	ND		0.01 ± 0.00 (2)	ND–0.01	0.05 ± 0.02 (3)	0.02–0.07
Arizona and New Mexico (western)	3	1.22 ± 1.03 (3)	0.16–3.28	0.02 ± 0.01 (2)	ND–0.04	0.01 ± 0.01 (2)	ND–0.03	0.04 ± 0.02 (2)	ND–0.07	0.27 ± 0.21 (3)	0.03–0.69

NOTE: Means and standard error were rounded off if the third place was five or more. Values in parentheses are number of pools that contained the residue. ND = not detected at 0.01 ppm.
[1] One or more of these pools contained fewer than 25 wings.

(Table 2). The highest level of dieldrin was 1.18 ppm in a pool from Alabama (Table 1). PCBs were detected in all pools from the Atlantic Flyway and were found in at least 90% of the pools from the other three flyways (Table 2). This is a significant increase ($P < 0.05$) in the percentage occurrence of PCBs over that reported for the 1976–77 hunting season (Table 2). The highest residues of PCBs were 1.80 ppm in a pool of black duck wings from New York and 1.62 ppm in a pool of mallard wings from North Carolina. Three pools from the Pacific Flyway, two from the Central Flyway, and one from the Mississippi Flyway did not have PCB residues at the 0.01-ppm limit of detection (Table 1).

In addition to the organochlorine compounds listed in Table 1, heptachlor epoxide, chlordane isomers, and hexachlorobenzene (HCB) were found in duck wings, but less frequently. Residues of these three compounds seldom exceeded 0.1 ppm, so these data were not included in Table 1. The percentage occurrence of these three compounds and the percentage occurrence of mirex and endrin are presented in Table 2 and compared with the 1976–77 wing data. Hexachlorocyclohexane, lindane, and toxaphene residues were found in only three pools at the 0.01-ppm level.

Means of DDE, DDT, TDE, dieldrin, and PCBs in the 1976 and 1979 collections are presented by flyways in Table 3. To compare these residues with the data pre-

TABLE 2. *Comparison of the percent occurrence of organochlorine residues in duck wings by flyway for the two collection periods of 1976–77 and 1979–80*

Species	Year of Collection	No. of Pools	Organochlorine Residues, ppm Wet Weight [1]								
			DDE	DDT	TDE	Dieldrin	PCBs	Heptachlor Epoxide	Mirex	Endrin	HCB	Chlordane Isomers
ATLANTIC FLYWAY												
Black duck	1976–1977 [2]	32	100_a [3]	69_a	66_a	84_a	100_a	34_a	19_a	3_a	16_a	59_a
Black duck	1979–1980	24	100_a	38_b	29_b	58_b	100_a	4_b	13_a	0_a	21_a	58_a
Mallard	1976–1977	20	100_a	60_a	50_a	85_a	100_a	50_a	50_a	5_a	10_a	55_a
Mallard	1979–1980	29	100_a	52_b	17_b	62_b	100_a	14_b	3_b	3_a	3_b	48_b
MISSISSIPPI FLYWAY												
Mallard	1976–1977	69	100_a	87_a	38_a	78_a	61_a	45_a	29_a	4_a	7_a	22_a
Mallard	1979–1980	64	100_a	28_b	13_b	64_b	98_b	28_b	2_b	8_b	2_b	16_a
CENTRAL FLYWAY												
Mallard	1976–1977	56	100_a	79_a	45_a	64_a	13_a	48_a	14_a	2_a	9_a	14_a
Mallard	1979–1980	54	100_a	22_b	2_b	22_b	90_b	30_b	0_b	0_a	4_b	7_b
PACIFIC FLYWAY												
Mallard	1976–1977	50	100_a	92_a	58_a	62_a	14_a	32_a	4_a	0_a	24_a	14_a
Mallard	1979–1980	44	100_a	57_b	7_b	39_b	93_b	23_b	0_a	0_a	23_a	5_b

[1] Detection limit = 0.01 ppm.
[2] Data taken from White *(8)*.
[3] 1979–80 percent occurrence is significantly different ($P < 0.05$) than 1976–77 percent occurrence where subscript letters (a or b) differ.

TABLE 3. *Means and standard errors of organochlorine residues in waterfowl wing pools by major flyway, 1976 and 1979*

Species	Flyway	Year	No. of Pools	Residues, ppm Wet Weight				
				DDE	DDT	TDE	Dieldrin	PCBs
Black duck	Atlantic	1976 [1]	32	0.39 ± 0.07 (32)	0.06 ± 0.01 (22)	0.03 ± 0.00 (21)	0.04 ± 0.01 (27)	0.52 ± 0.08 (32)
		1979	24	0.32 ± 0.04 (24)	0.02 ± 0.00 (9)	0.04 ± 0.03 (7)	0.03 ± 0.01 (14)	0.63 ± 0.09 (24)
Mallard	Atlantic	1976	20	0.32 ± 0.07 (20)	0.07 ± 0.01 (12)	0.02 ± 0.01 (10)	0.06 ± 0.03 (17)	0.52 ± 0.18 (20)
		1979	29	0.27 ± 0.03 (29)	0.02 ± 0.01 (15)	0.01 ± 0.00 (5)	0.05 ± 0.03 (18)	0.45 ± 0.07 (29)
Mallard	Mississippi	1976	69	0.25 ± 0.04 (69)	0.07 ± 0.01 (60)	0.05 ± 0.03 (26)	0.05 ± 0.01 (54)	0.23 ± 0.03 (42)
		1979	64	0.17 ± 0.03 (64)	0.05 ± 0.01 (18)	0.05 ± 0.02 (8)	0.05 ± 0.03 (41)	0.11 ± 0.02 (63)
Mallard	Central	1976	56	0.28 ± 0.17 (56)	0.05 ± 0.01 (44)	0.04 ± 0.01 (25)	0.03 ± 0.01 (36)	0.15 ± 0.01 (7)
		1979	54	0.10 ± 0.02 (54)	0.03 ± 0.01 (12)	0.02 ± 0.00 (1)	0.02 ± 0.00 (12)	0.06 ± 0.01 (49)
Mallard	Pacific	1976	50	0.22 ± 0.04 (50)	0.06 ± 0.01 [2] (46)	0.03 ± 0.00 (29)	0.02 ± 0.00 (31)	0.16 ± 0.04 (7)
		1979	44	0.35 ± 0.08 (44)	0.02 ± 0.01 (25)	0.02 ± 0.01 (3)	0.02 ± 0.00 (17)	0.07 ± 0.02 (41)

NOTE: Values in parentheses are actual number of pools containing residues; means were calculated using these values.
[1] Data taken from White *(8)*.
[2] Significant difference ($P < 0.05$).

sented from the 1976 collection (*8*), the author calculated the mean values by using only the wing pools that contained the residues. A trend toward lower mean values for most of these residues in both the mallard and black duck wings was not significant ($P > 0.05$).

The only significant decline ($P < 0.05$) was DDT residues in mallard wings from the Pacific Flyway (Table 3). Residues of DDT, TDE, and dieldrin were all low in the four flyways, and the percentage occurrence of these contaminants has declined significantly ($P < 0.05$) since 1976. PCB residues were low in mallard wings from the Mississippi, Central, and Pacific Flyways, but their percentage occurrence increased significantly ($P < 0.05$) above the 1976 level (Table 2).

Conclusions

Mean values of DDE residues in mallard and black duck were not significantly ($P > 0.05$) lower than those reported for 1976 in all flyways. DDT, TDE, and dieldrin residues in duck wings have declined significantly ($P < 0.05$) in the percentage occurrence in all flyways. The decline of PCB residues in mallard wings from all flyways was not significant ($P > 0.05$). PCBs, however, occurred in a significantly ($P < 0.05$) larger percent of the 1979–80 pools than in the 1976 pools.

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HUMANS

Organochlorine Pesticide Residues in Human Milk Samples from Comarca Lagunera, Mexico, 1976

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ABSTRACT

Milk samples were obtained from 15 nursing mothers in the agricultural region of Comarca Lagunera, Mexico, and were analyzed for organochlorine pesticide residues. Nine different types of residues were found. Of these, p,p'-DDE, p,p'-DDT, and β-BHC occurred most frequently. All samples had concentrations of DDT-derived compounds higher than the practical limit recommended by the U.N. Food and Agriculture Organization/World Health Organization for DDT in cows' milk. Residues of other chlorinated hydrocarbons were present at levels similar to those found in human milk in other developing countries.

Introduction

In the developing countries, organochlorine pesticides are used in large quantities to control agricultural pests and the vectors of endemic diseases. Although there have been few studies to determine organochlorine residues in human milk samples, some studies have been carried out in Guatemala (*20, 28*), Portugal (*12*), and Argentina (*10*).

In spite of high production, import, and use of these compounds in Mexico, there had been no studies of their presence in human milk. The present study is a preliminary evaluation of those residues in human milk from Comarca Lagunera. This is an important agricultural region of Mexico, on the border of the states of Durango and Coahuila, where the principal crop is cotton.

Comarca Lagunera was selected because previous analyses have shown consistently high levels of organochlorine pesticide residues in foodstuffs and animal feeds (*3, 4*) and in human adipose tissue (*2*).

Methods and Materials

All solvents were distilled twice in all-glass systems and checked by a 100-fold concentration test. Florisil was standardized for oil retention ability and activity. Before use, all reagents were checked for electron-capturing impurities.

Fifteen human milk samples were collected during March 1976 from voluntary donors at the University Hospital in Torreón, the main city of Comarca. All donors had lived in the area for 4 or more years. Four donors were from medium-income homes and 11 were from low socioeconomic levels. Seven lived in urban areas and eight lived in rural areas of Comarca. Donors' ages ranged from 16 to 30 years, with infants ranging in age from 1 to 29 days. All samples were manually expressed directly into wide-mouth jars that had been thoroughly cleaned. Jars were closed with Teflon-lined caps and stored in a refrigerator until samples were analyzed.

Lipids were extracted at the School of Medicine in Torreón immediately after sampling was completed. The volume of each sample was measured and the lipids were extracted with a BD-1 solution (*15*) at 3:2 (v/v) sample:solution ratio. Extracted lipids were carefully transferred to clean vials and weighed. Extractable lipids averaged 1.91% ± 0.97%. Lipids were frozen and taken to the CIEA-IPN laboratories in Mexico City, where they were kept at −20°C until analysis.

Three sets of analyses were carried out; each was comprised of five samples. Along with each set, a blank and a sample of milk lipids fortified with 1 ppm β-BHC

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and 3.5 ppm *p,p'*-DDE (lipid basis) were also analyzed. Recoveries ranged from 96% to 103%.

The lipids were dissolved in *n*-hexane and transferred to a chromatographic column prepared with 10 g Florisil deactivated with 2% water. The column was eluted with 100 ml of a 70:30 (v/v) mixture of petroleum ether–CH_2Cl_2 (*7*). The eluate was concentrated carefully and the residue was dissolved in *n*-hexane for gas-liquid chromatographic (GLC) analysis. No further cleanup was necessary.

Identification and quantitation were carried out by GLC under the following conditions:

Chromatographs:	Varian Aerograph, Models 1440 and 2440
Detectors:	electron-capture tritium and scandium tritiide
Columns:	glass, 6-ft long by 2-mm ID, packed with either (a) 3% OV-101 or (b) 3% OV-210, both on 100–120-mesh Gas-Chrom Q
Temperatures:	column (a) 170°C column (b) 150°C
Carrier gas:	high-purity nitrogen flowing through (a) at 40 ml/min and through (b) at 35 ml/min

Qualitative identification was accomplished by comparison of retention times with those of known standards provided by the U.S. Environmental Protection Agency. Quantitation was based on relative peak heights of individual standard solutions of each compound. The minimum detectable level was 0.005 μg/g (extractable-lipid basis) for all compounds.

Identity was confirmed routinely by the multicolumn technique (*11*), using a column packed with a mixture of 2% QF-1 and 2% SE-30 on 100–120-mesh Gas-Chrom Q. Column temperature was 150°C and carrier gas was nitrogen flowing at 35 ml/min. All samples containing more than 0.5 μg/g (extractable-lipid basis) of *p,p'*-DDE and *p,p'*-DDT were confirmed by chemical derivation (*8*) and by thin-layer chromatography (TLC) (*7*). Samples containing above 0.2 μg β-BHC/g were confirmed only by TLC.

Results and Discussion

The number of chlorinated hydrocarbon residues per sample ranged from five to nine, with five to six compounds per sample occurring most often.

The following compounds were identified: hexachlorobenzene, α-BHC, β-BHC, *p,p'*-DDE, *p,p'*-TDE, *p,p'*-DDT, dieldrin, endrin, and heptachlor epoxide. Those found more frequently in concentrations higher than 0.01 μg/g were β-BHC, *p,p'*-DDE, and *p,p'*-DDT. However, *p,p'*-DDT was found in only 11 samples, whereas *p,p'*-DDE was present in all samples. Hexachlorobenzene and *p,p'*-TDE occurred at concentrations above 0.01 μg/g in only four and five samples, respectively; dieldrin, heptachlor expoxide, α-BHC, and endrin were found only in trace concentrations—below 0.01 μg/g. Among these, the most frequent was dieldrin, which was identified in 13 samples, and heptachlor epoxide, which was present in 7. These data are summarized in Table 1.

The means, ranges, and standard deviations for these compounds are presented in Table 2. These data are calculated both on an extractable-lipid basis (μg/g) and in whole milk (μg/ml). Only the results from samples with more than 0.01 μg/g of a given compound were considered for these calculations. Total equivalent DDT was obtained by multiplying the values for *p,p'*-DDE and *p,p'*-TDE by the appropriate factors before addition.

Among the compounds with high percent occurrences, *p,p'*-DDE was found at the highest mean concentration,

TABLE 1. *Occurrence of organochlorine pesticide residues in human milk samples from Comarca Lagunera, Mexico, 1976*

Compound	Total Positive Samples		Samples with Residue Levels Above 0.01 μg/g	
	n/N	%	n/N	%
Hexachlorobenzene	9/15	60	4/15	27
α-BHC	4/15	27	—	—
β-BHC	15/15	100	15/15	100
Dieldrin	13/15	87	—	—
Endrin	2/15	13	—	—
Heptachlor epoxide	7/15	47	—	—
p,p'-DDE	15/15	100	15/15	100
p,p'-DDT	15/15	100	11/15	73
p,p'-TDE	15/15	100	5/15	33

NOTE: n = number of positive samples; N = total number of samples.

TABLE 2. *Concentrations of organochlorine pesticide residues in human milk samples from Comarca Lagunera, Mexico, 1976* [1]

Compound	Concentrations of Residues μg/g	
	Extractable Lipid	Whole Milk
	$\bar{x}$ ± SD (Range)	$\bar{x}$ ± SD (Range)
Hexachlorobenzene	0.21 ± 0.23 (ND–0.48)	0.002 ± 0.002 (ND–0.004)
β-BHC	1.63 ± 0.94 (0.46–3.58)	0.030 ± 0.026 (0.007–0.100)
p,p'-DDE	10.35 ± 11.02 (1.36–36.01)	0.202 ± 0.266 (0.013–0.984)
p,p'-DDT	1.98 ± 1.70 (T–6.04)	0.049 ± 0.073 (T–0.243)
p,p'-TDE	0.56 ± 0.37 (T–1.06)	0.015 ± 0.016 (T–0.043)
Total Equiv. DDT [2]	13.18 ± 13.39 (1.51–43.86)	0.266 ± 0.348 (0.020–1.198)

NOTE: $\bar{x}$ = mean concentration; SD = standard deviation; ND = <0.005 μg/g extractable lipids; T = Trace (0.01 μg/g >T>0.005 μg/g extractable lipids).

[1] Calculations based on samples with residues >0.01 μg/g extractable lipids.

[2] DDT + 1.115 DDE + 1.11 TDE.

followed by *p,p'*-DDT and β-BHC. Total equivalent DDT ranged from 1.21 to 35.09 times the practical limit (1.25 μg/g, lipid basis) recommended by FAO/WHO for DDT alone or combined with TDE and DDE in cows' milk (*26*); the mean concentration of *p,p'*-DDT was 1.98 μg/g, 1.58 times the FAO/WHO limit. The concentrations of *p,p'*-DDE ranged from 1.08 to 28.81 times the limit. Therefore, concentrations of DDT-derived compounds in all samples were higher than the FAO/WHO practical limit. The mean concentration of β-BHC (1.63 μg/g) was equivalent to 8.15 times the limit of 0.2 μg/g recommended by FAO/WHO for the δ-isomer (lindane) in cows' milk (*26*). β-BHC was above this limit in all samples.

The finding of residues of the cyclodienic compounds dieldrin, heptachlor epoxide, and endrin in the human milks analyzed, although at low levels, is a matter of concern. These pesticides are being increasingly used in Mexico, even though their persistence and toxicological effects have caused their use to be severely restricted in other countries.

Also noteworthy is the presence of hexachlorobenzene residue, which heretofore has only been reported in developed countries (*1, 17, 22, 23*).

The mean value (lipid basis) of *p,p'*-DDE calculated as DDT (11.81 μg/g) represented 89.60% of the average total equivalent DDT. This could indicate that most of the DDT-derived material in the human milks analyzed originated in the food chain due to excessive past use of DDT in the region (*5*).

In general, the organochlorine residue levels found in the present study of human milk would be unacceptable in cows' milk in other countries.

The results of the present study and similar surveys in other countries are presented in Table 3. It is evident that the higher values for *p,p'*-DDE, β-BHC, and total equivalent DDT in human milk correspond to levels found in other developing countries such as Guatemala, Portugal, Argentina, and Chile.

Several other studies (*9, 19*) have indicated that high concentrations of organochlorine residues in human milk may adversely affect neonates. Other investigators have shown the effects of the chronic ingestion of low levels of some pesticides are more severe in young and malnourished animals (*6, 16*).

Mother's milk is an important source of nutrition for infants in the region studied, especially in the low socioeconomic groups in which malnourishment of mother and child is also frequent. In view of the high values obtained for organochlorine pesticide residues in human milk in the present study, further related research in this region and throughout Mexico is essential.

Acknowledgments

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TABLE 3. *Average concentrations of some organochlorine pesticide residues in human milk from various countries, 1965–79*

Country	Year	Concentrations in Whole Milk, μg/ml			
		β-BHC	*p,p'*-DDE	*p,p'*-DDT	Total Equiv. DDT
United States (*21*)	1965	—	—	0.08	0.12
Holland (*25*)	1971	0.004	0.03	0.016	—
Australia (*23*)	1975	—	0.080	0.015	—
Sweden (*27*)	1972	—	0.059	0.020	—
United States (*14*)	1977	0.003	0.035	0.008	—
Canada (New Brunswick) (*18*)	1974	—	0.035	0.013	—
Canada (*17*)	1979	0.002	0.035	0.006	—
New Guinea (Sepik) (*13*)	1972	—	0.096	0.181	—
New Guinea (Saidor) (*13*)	1972	—	0.002	0.001	—
Portugal (Lisbon) (*12*)	1974	—	0.223	0.100	0.323
Portugal (Bragança) (*12*)	1974	—	0.040	0.023	0.063
Guatemala (La Bomba) (*20*)	1973	—	1.02	1.00	2.15
Guatemala (La Bomba) (*20*)	1976	—	—	—	0.587
Guatemala (Guatemala City) (*??*)	1976	—	—	—	0.233
Argentina (*10*)	1974	0.042	0.092	0.046	0.140
Chile (*24*)	1978	—	0.15	0.092	0.25
Mexico (This Study)	—	0.030	0.202	0.049	0.266

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WATER

1,2-Dibromo-3-chloropropane Residues in Water in South Carolina, 1979–80[1]

George E. Carter, Jr., and Melissa B. Riley [2]

ABSTRACT

During 1979–80, a total of 236 water samples were collected from 205 sites in South Carolina. Well water, surface water (lakes, ponds, and rivers), and municipal water were sampled and analyzed for the soil fumigant 1,2–dibromo–3–chloropropane (DBCP). DBCP levels ranged from nondetectable to 0.05 μg/liter (ppb) in an area of nonuse (background). No municipal water samples in the state exceeded the background level. In the area of high use of DBCP, 37% of the surface water samples exceeded the background level, but none exceeded 0.4 μg/liter. Twenty-seven percent of the well water samples from the high-use area exceeding the background level, and 10.2% of the samples exceeded 1 μg/liter. All samples exceeding 1 μg/liter came from a small area within one county. The possible mode of contamination was not determined.

Introduction

Soil fumigation for nematode control is a key factor in a program against peach tree short life, a condition that has decimated southeastern peach orchards (*1, 5*). Both pre- and postplant treatments are required for growing healthy peach trees (*Prunus persica* (L.) Batsch) (*3*). 1,2-Dibromo-3-chloropropane (DBCP) is the postplant nematicide used to control ring *(Macroposthonia xenoplax Raski)* and root-knot *(Meloidogyne spp.)* nematodes. Peach trees have no resistance to either nematode, DBCP is the only pesticide cleared for postplant treatment of orchards, and no other pesticide has been effective for controlling the nematodes well enough to prevent premature death of peach trees. Low concentrations of DBCP have been reported in California groundwater samples (*4*), which led to questions of groundwater contamination in South Carolina. The purpose of the present study was to determine the levels of DBCP present in water samples collected in South Carolina.

Materials and Methods

WATER SAMPLE COLLECTION

Three areas of South Carolina were selected for their DBCP usage: (1) Piedmont area, non-use; (2) Coastal area, scattered agricultural use; and (3) Sandridge area, extensive agricultural use. During 1979–80, three types of water samples were collected from each area as follows: well water from privately owned wells; surface water from ponds, rivers, and lakes; and water from homes supplied by municipal sources. Samples were collected in new canning jars which were discarded after one collection. Jars were rinsed with glass-distilled, pesticide grade ethyl acetate, covered with ethyl acetate-rinsed aluminum foil, and closed with jar caps and rings. Jars were filled to the top from home taps (well and municipal) or by submerging into ponds, rivers, and lakes, leaving no head space, and were placed in ice immediately after collection. The location of the sample and any information on the agricultural practices of the area were recorded at the time of collection. Sites yielding samples containing over 1 ppb DBCP were resampled to verify results.

EXTRACTION

This procedure was obtained from the California Department of Food and Agriculture (*2*) and was modified by the addition of a centrifugation step. Five glass beads, rinsed with ethyl acetate, were combined with a 160-ml water sample and 10-ml glass-distilled, pesticide-grade ethyl acetate in a round-bottom boiling flask that was attached to a modified Stark and Dean trap and condenser. The flask was placed in a heating mantle; full voltage was applied until the mixture began to boil and then was reduced to one-third maximum. The mixture was allowed to reflux 15 minutes or until the ethyl acetate was distilled over to the trap. The

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heating mantle was turned off and the condenser was washed with distilled water. After 5 minutes, the distillate was removed and centrifuged 10 minutes at 17, 500g in a Sorvall RC2-B refrigerated centrifuge. The ethyl acetate layer was transferred to an ethyl acetate-washed, screw-cap tube to which a small amount of anhydrous sodium sulfate was added. An aluminum foil liner rinsed with ethyl acetate was placed between the test tube and the screw cap. Samples were kept in the freezer after extraction and before gas chromatographic analysis.

Glassware blanks were run by placing 30 ml ethyl acetate in the boiling flask of the extraction apparatus and refluxing it 15 minutes. A 10-ml quantity was then collected to be used as a glassware blank. Glassware was cleaned by placing it overnight in sodium dichromate–sulfuric acid cleaning solution, and then rinsing it three times with distilled water and ethyl acetate.

GAS CHROMATOGRAPHY

The concentration of DBCP in water samples was determined by use of a Varian 3700 gas chromatograph connected to a CDS111 chromatography data system and recorder. Instrument parameters and operating conditions were as follows:

Detector:	^{63}Ni electron-capture
Column	2 m by 2 mm glass, packed with 10% OV-101 on 80–100-mesh Chromosorb W-HP
Temperatures:	column: 100°C for 3 min, then increased column: 4°/min for 7 min, then increased column: 18°/min for 5.66 min, and then held column: at 230°C for 4.33 min injector 220°C detector 280°C
Carrier gas:	nitrogen flowing at 30 ml/min
Retention time:	5.75 minutes for DBCP
Detection limit:	0.008 ppb

Recovery percentage was determined from the mean value of four fortified samples (50 ng DBCP added to 160 ml distilled, deionized water). This value, 88%, was used to calculate DBCP present in the samples. Levels of DBCP were calculated by the data system, using an external standard method of calibration.

DBCP standards were prepared in ethyl acetate, using a 99.6% pure analytical standard (AMVAC Chemical Corp.); standards and sample extracts were kept in different freezers. The gas chromatograph was calibrated using a 5 pg DBCP/μl standard as the first sample every day. Ethyl acetate blanks were run after every sample containing DBCP.

Either of the following apparatus and operating conditions was used to confirm the presence of DBCP:

Column:	2 m by 2 mm glass, packed with 3% OV-210 on 80–100-mesh Chromosorb W-HP
Temperatures, °C	column 75 injector 270 detector 250
DBCP retention time:	2.1 min
OR	
Column:	2 m by 2 mm glass, packed with 2% DEGS on 80–100-mesh Chromosorb W, A/W
Temperatures, °C	column 100 injector 250 detector 250
DBCP retention time:	1.2 min
Carrier gas (both columns):	nitrogen flowing at 40 ml/min
Detection limit (both)	0.008 ppb

MASS SPECTROMETRIC ANALYSIS FOR DBCP

Selected samples were taken to Research Triangle Institute in Research Triangle Park, North Carolina, for analysis. Methane-enhanced negative ion chemical ionization mass spectrometric analysis was conducted on one of two gas chromatograph-mass spectrometers under the following conditions:

GC/MS:	LKB 2091
Column:	25-m WCOT SE-30 capillary
Temperatures, °C:	column: 100°C for 4 min, then 8° min to 240°C injector 210 ion source 210
Electron energy:	50 eV
Box current:	250 μA
Accelerating voltage:	3.5 kV
OR	
GC/MS:	Finnigan Model 4000/PPNICI
Column:	25-m SP2100 capillary
Temperatures, °C:	column 70° for 1 min, then 8°/min to 250°C injector 250 ion source 250
Electron energy:	70 eV

The appearance of the characteristic ions (m/z 79, 81, 158, 160, and 162) in the correct retention window was used to confirm the presence of DBCP in the samples. Tentative confirmation was based on the observation of the m/z 79 and 81 ions in the correct retention window. Selected samples were concentrated before analysis by placing the sample in ice with a stream of nitrogen flowing over it.

Results and Discussion

Distribution of the 236 water samples is shown in Table 1. Samples from the Piedmont area (non-use of DBCP) appeared to contain a background level of DBCP or a compound indistinguishable from DBCP at levels from 0.008 ppb (limit of detection) to 0.05

TABLE 1. *Distribution of water samples analyzed for DBCP in South Carolina, 1979–80*

Area	Type of Water	No. of Sites	No. of Samples
Piedmont	well	8	8
(Non-use)	surface	15	18
	municipal	3	3
Sandridge	well	49	63
(High use)	surface	46	60
	municipal	8	8
Coastal	well	24	24
(Scattered use)	surface	33	33
	municipal	19	19

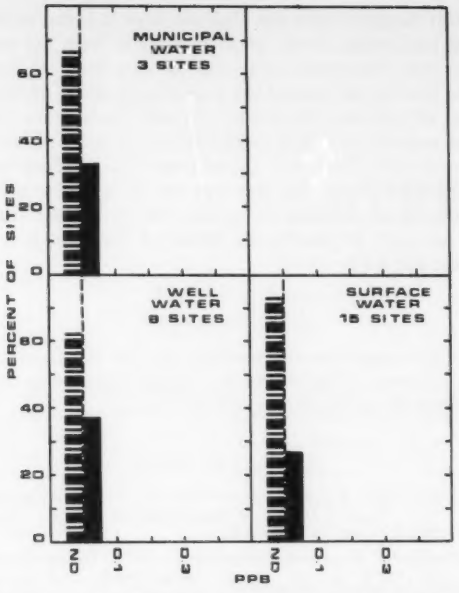

FIGURE 1. *Percentage of sites showing DBCP contamination (ppb) in Piedmont area of South Carolina. Detection limit = 0.008 ppb. ND represents no detectable residue of DBCP.*

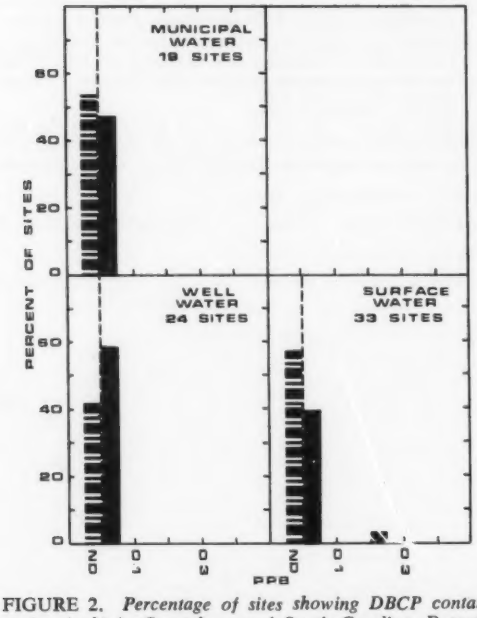

FIGURE 2. *Percentage of sites showing DBCP contamination (ppb) in Coastal area of South Carolina. Detection limit = 0.008 ppb. ND represents no detectable residue of DBCP.*

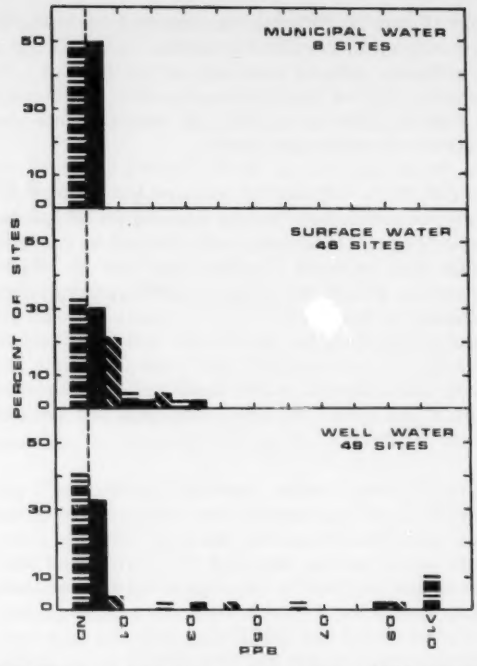

FIGURE 3. *Percentage of sites showing DBCP contamination (ppb) in Sandridge area of South Carolina. Detection limit = 0.008 ppb. ND represents no detectable residue of DBCP.*

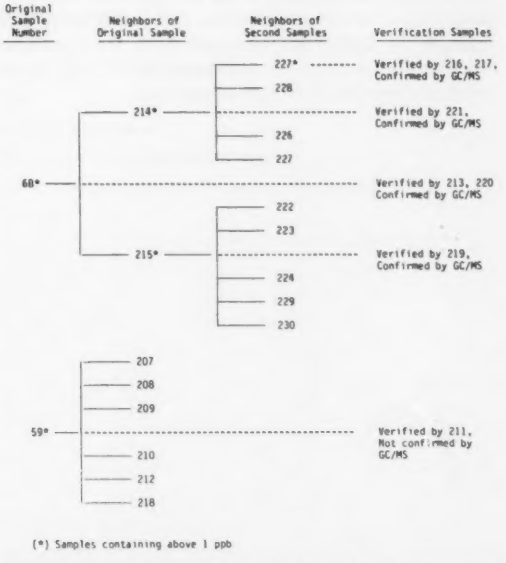

FIGURE 4. *Treatment of original water samples containing above 1 ppb DBCP (numbers indicate sample numbers).*

ppb (Figure 1). Although the compound was tested under two sets of gas chromatographic conditions and at significantly different polarities, and on the mass spectrometer, the low level prevented positive identification. Levels of DBCP up to 0.05 ppb were therefore considered to be background levels.

In the coastal area of South Carolina (scattered use of DBCP), no well water or municipal water sample and only one surface water sample exceeded the background level (Figure 2). Samples were obtained in the Sandridge area of South Carolina (high use of DBCP) showed a greater variability in DBCP concentrations (Figure 3). No municipal water sample exceeded the background level, but surface and well water samples varied from none to more than 1 ppb. Seventeen surface water samples in the Sandridge area contained DBCP, but none were above 0.04 ppb, and 10 were below 0.1 ppb.

Five well water samples contained greater than 1 ppb DBCP. All of these samples were verified by resampling at a later date. Two of the sites were located in a random survey, and the remaining three were found when the nearest neighbors to the original samples were sampled, as shown in Figure 4. When the samples containing more than 1 ppb DBCP were tested by mass spectrometry, four of the five were confirmed to contain DBCP.

This study indicates that low levels of a material that is indistinguishable from DBCP may exist in groundwater where no agricultural use has occurred. This possibility must be considered when data concerning trace amounts of DBCP are analyzed. One must consider whether the material is authentic DBCP and, if so, whether it resulted from agricultural use.

Most samples from the high-use area did not exceed the background levels found in samples from the nonuse area, but several well water samples from the high-use locality did exceed the background levels. Hydrology of the area, the nature of well construction, and use patterns of DBCP in the vicinity of the wells were not studied. Therefore, it is impossible to conclude that contamination in this area was due to agricultural application of products containing DBCP. Further study is necessary to identify the source of contamination in these five wells.

Acknowledgments

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APPENDIX

Chemical Names of Compounds Discussed in This Issue

ALACHLOR	2-Chloro-2′,6′-diethyl-*N*-(methoxymethyl)acetanilide
ALDRIN	Hexachlorohexahydro-*endo, exo*-dimethanonaphthalene 95% and related compounds 5%
AROCLOR 1016 or 1242	PCB, approximately 42% chlorine
AROCLOR 1242	PCB, approximately 42% chlorine
AROCLOR 1246	PCB, approximately 46% chlorine
AROCLOR 1254	PCB, approximately 54% chlorine
ATRAZ'NE	2-Chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine
BHC (Benzene Hexachloride)	1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers)
CHLORDANE	Technical: 60% octachloro-4,7-methanotetrahydroindane and 40% related compounds
CYANAZINE	2-[[4-Chloro-6-(ethylamino)-*s*-triazin-2-yl]amino]-2-methylpropionitrile
DDE	Dichlorodiphenyldichloroethylene (degradation product of DDT)
DDT	Dichloro diphenyl trichloroethane. Principal isomer present (*p,p′*-DDT; not less than 70%): 1,1,1-trichloro-2,2,-bis(*p*-chlorophenyl)ethane
DIELDRIN	Hexachloroepoxyoctahydro-*endo,exo*-dimethanonaphthalene 85% and related compounds 15%
ENDRIN	Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene
HCB	Hexachlorobenzene
HEPTACHLOR EPOXIDE	1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan
LINDANE	*Gamma* isomer of benzene hexachloride (BHC)
MIREX	Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene
PCBs (Polychlorinated Biphenyls)	Mixtures of chlorinated biphenyl compounds having various percentages of chlorine
TDE	Dichloro diphenyl dichloroethane (1,1-dichloro-2,2-bis (*p*-chlorophenyl)ethane, principal component)
TOXAPHENE	Technical chlorinated camphene (67-69% chlorine)

ERRATUM

Pesticides Monitoring Journal, Volume 15, Number 2, page 78, of the article "Chlorinated Hydrocarbon Pesticides in Blood of Newborn Babies in India" by M. K. J. Siddiqui et al. Line 9 in the right column and Tables 1–3 should be corrected to read as follows:

There was a significant difference ($P < 0.005$) in total DDT residues by area of residence, but a slightly higher concentration of DDE was estimated in urban subjects, . . .

TABLE 1. *Organochlorine pesticides detected (ppb) in cord blood collected at term from 100 pregnant women, by age group*

Pesticides Detected	Women 18–25 Years Old (58 Cases)			Women 26–34 Years Old (42 Cases)		
	Range	Arithmetic Mean	SE	Range	Arithmetic Mean	SE
Total BHC	6.9–278.3	32.97	16.89	2.0–507.84	45.79	5.90
Lindane*	1.28–78.69	10.27	2.13	3.10–175.73	14.99	1.23
p,p'-DDE	1.02–850.0	12.33	1.98	2.05–78.14	23.10	4.75
p,p'-DDD	ND–48.21	5.84	1.25	ND–48.21	8.01	2.85
p,p'-DDT**	ND–140.0	7.30	2.32	ND–57.52	22.13	2.37
ΣDDT[1]	2.73–1029.85	59.65	25.51	4.59–149.62	51.18	8.51

*, ** Statistically significant ($P<0.05$ and 0.005, respectively).
[1] ΣDDT=total DDT equivalent.

TABLE 2. *Organochlorine pesticides detected (ppb) in cord blood collected at term from 100 pregnant women, by dietetic habit*

Pesticides Detected	Vegetarian Diet (36 Cases)			Nonvegetarian Diet (64 Cases)		
	Range	Arithmetic Mean	SE	Range	Arithmetic Mean	SE
Total BHC	6.9–278.43	38.3	7.29	2.0–507.84	35.64	3.13
Lindane	1.28–78.68	12.47	0.34	1.8–175.73	11.41	1.10
p,p'-DDE	1.02–850.0	15.33	3.26	1.9–150.0	20.53	4.39
p,p'-DDD	ND–48.21	6.55	1.85	0.89–32.09	8.49	1.80
p,p'-DDT	ND–55.56	14.89	3.05	1.78–140.0	17.08	3.55
ΣDDT	4.03–1029.85	62.22	8.50	2.73–240.41	50.07	7.78

TABLE 3. *Organochlorine pesticides detected (ppb) in cord blood collected at term from 100 pregnant women, by area of residence*

Detected Pesticides	Urban Population (48 Cases)			Rural Population (52 Cases)		
	Range	Arithmetic Mean	SE	Range	Arithmetic Mean	SE
Total BHC*	2.0–507.84	47.38	13.87	3.0–76.97	27.06	2.31
Lindane**	1.28–175.73	16.94	0.72	1.8–33.43	8.88	1.63
p,p'-DDE	1.02–257.50	22.81	7.05	2.2–850.0	15.48	4.38
p,p'-DDD	ND–48.21	7.33	3.88	ND–32.09	6.25	1.43
p,p'-DDT	0.5–50.23	13.71	2.19	ND–140.0	17.08	4.43
ΣDDT***	2.73–338.43	41.60	10.88	7.14–1029.85	68.23	13.84

*, **, *** Statistically significant ($P<0.05$, 0.05, and 0.005, respectively).

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